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Direct Conversion of CO₂ to Solid Carbon by Ga-Based Liquid Metals[†]

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The direct conversion of CO₂ to carbon is a highly providential route; however, conventional thermal and catalytic approaches are hindered by high energy demands and are limited by coking. Here, we report a robust and highly selective method for the direct conversion of CO₂ to solid carbon over EGaln liquid metal (LM) alloy. We utilized the low-melting point of this alloy to facilitate the reduction of CO₂ at low temperatures, producing 319 μmol/hr of carbon at 200°C, and remarkably enabling CO₂ activation and carbon production even at room temperature, without the use of a supplementary reductant such as hydrogen. The deployed LM showed no signs of deactivation by coking and the generated carbon is shown to naturally accumulate at the top of the LM where it can be easily collected. In-situ XPS measurements indicate an increase of 9.6% in the carbon-carbon bond content and an equivalent decrease in the Ga metal content, upon exposure of the LM to CO₂ for 30 mins at 200°C and 1 bar. This led to the conclusion that solid carbon and gallium oxide are the final reaction products of this process. Density functional theory calculations shed further light on the adsorption and dissociation of CO₂ over Ga and EGaln. The presented method creates a pathway to transforming CO₂ to perpetually stored solid carbon and can therefore set a trajectory for making a measurable impact on carbon intensive industries.

Introduction

As far as devising carbon dioxide conversion processes go, thermal approaches provide a viable pathway toward effectively driv-

ing the decomposition reaction for the production of carbon. CO₂ is not only the most common greenhouse gas released into the environment but is also the most stable state of carbon.¹ Due to the high thermal stability of CO₂, its dissociation requires extremely high operating temperatures (>2000 K).² Moreover, current dependencies on solid heterogeneous catalysts mean that the generation of solid carbon products typically results in rapid catalyst deactivation due to coking. Therefore, processes aimed at the direct decomposition of CO₂ (CO₂→C+O₂) for the production of carbon are scarce. Existing methods focusing on the decomposition reaction, are typically limited by one or a combination of: the use of solid catalysts,^{3,4} the reliance on the expenditure of hydrogen as a reducing agent,⁵ and the need for external energy input to thermally drive the dissociation of the CO₂ molecule.⁶ Other alternative strategies have focused on the use of alternative energy sources to heat; in the form of plasma technologies,⁷ and photocatalytic^{5,8} or electrocatalytic^{9–11} reduction routes which remain hinged on further technological advancements, particularly in terms of scaled operations. Furthermore, conventional decomposition methods that predominantly rely on heterogeneous catalysts suffer from low conversion efficiencies.^{12,13} This restricts studies to focus on intermittent CO₂ conversion in the form of batch processing.

Liquid metals (LM) have recently gained traction in the catalysis space, owing to their unique physicochemical properties and high catalytic activities.¹⁴ In particular, the existence of LMs in the liquid phase, their high thermal and electrical conductivity, high thermal stability, and exceptional resistance to coking make LMs promising candidates not only for catalysis but also other applications including flexible circuits, self-healing superconductors and energy storage applications.^{14–17} Moreover, Ga-based LMs can dissolve other metals to form a range of alloys in varying compositions.¹⁸ This feature is critical for the development of innovative material formulations with targeted properties and designed functionality.¹⁴ On that account, LM catalysts have been successfully utilized in alkane dehydrogenation reactions, predominantly

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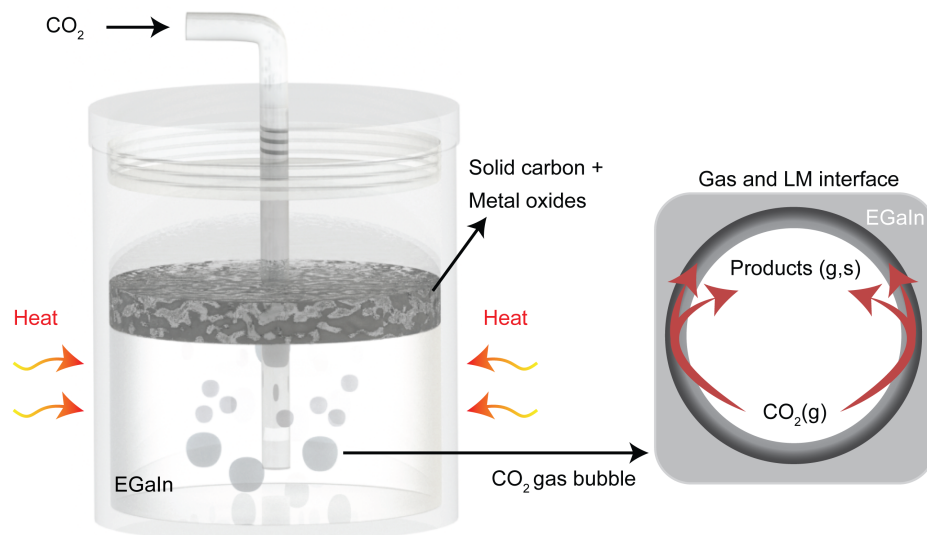


Fig. 1 Overview of the CO₂ dissociation process over liquid EGaIn. Representation of the interaction between gaseous CO₂ and the molten metal for the production of solid carbon and the ensuing generation of Ga oxide is shown on the right.

in methane pyrolysis,^{19,20} and propane and butane dehydrogenation schemes.²¹ The deployment of LMs has thus demonstrated exceptional effectiveness in producing H₂ and solid carbon from alkanes without coking or loss in catalytic activity.²² The advantageous use of LMs has also been demonstrated in an electrochemical CO₂ reduction approach,¹¹ which although inherently constrained in the amount of carbon it can produce, uncovers the effectiveness of LMs and signposts their viability in CO₂ reduction. Hence, combined with a compelling need for materials that are resistant to coking, the demand for highly active materials that can address persisting environmental and industrial challenges make LMs promising candidates for energy and environmental applications, particularly where solid carbon generation is favorable such as in CO₂ splitting processes.

In this study, we report a new method for the continuous direct decomposition of CO₂ to solid carbon and oxygen by employing a liquid metal (LM) alloy. We also show that the decomposition of CO₂ over a eutectic of gallium and indium (EGaIn) can be achieved at near room temperature. Here, we demonstrate an approach that enhances carbon separation and collection due to the low solubility of carbon in the LM melt and the high buoyancy of carbon on molten metal. The focus of this work is on breaking the concomitant energy restrictions of dissociating stable CO₂ molecules, by operating the reaction at temperatures between 25°C and 500°C. The process reported provides an alternative pathway of splitting CO₂, independent of the use of intense heat or hydrogen for the reduction of CO₂. Moreover, in addition to the relative simplicity of the process, the robustness and high activity of the LM, and the high efficiency for carbon production indicate that the performance of the LM remains uncompromised.

Results and Discussions

The CO₂ reduction process is designed to utilize low melting point LMs that enable operating within a region of far milder conditions from those where CO₂ naturally starts to decompose. Hence

EGaIn, composed of 75 wt.% Ga and 25 wt.% In, is used due to its low melting point (15.5°C) and the ability to retain its liquid state at room temperature.²³ Furthermore, the use of EGaIn for the decomposition offers an added advantage due to the simplicity of its preparation method, ease of batch-to-batch reproducibility and ease of scaling up production. The prepared EGaIn alloy (see methods in ESI†) was applied in a bubbling column reactor to test its activity, as illustrated in Fig. 1. The experimental setup allows for sufficient gas-liquid contact, establishes a medium for the CO₂ splitting reaction, and facilitates carbon collection (Fig. S1, ESI†). Due to the insolubility of carbon in the LM melt, and the density difference between the produced carbon and the LM, the carbon accumulates at the top of the melt (Fig. S2, ESI†).

The activity of the LM was appraised in a 30 cm bubbling column reactor under a continuous flow of gaseous CO₂ feed (balanced at a 1:2 ratio with Ar). While feeding pure CO₂ is expected to enhance the mass transfer in the reaction, the CO₂ feed was balanced with Ar to enable operating within the detection range of the online gas chromatograph. Tests were carried out at ambient pressure and focus was limited to low operating temperatures (below 400°C). The thermal activity of EGaIn for CO₂ conversion at 200°C was observed to increase as a function of time for a period of 150 minutes, and proceeded to reach a steady carbon production rate of 319 μmol/hr (Fig. 2a). Apart from the unconsumed CO₂, no other gaseous products were detected in the reactor effluent. Notably, similar conversion using pure Ga was observed in control runs (Fig. S3, ESI†). The efficacy of pure Ga is not unexpected since Ga exhibits a higher reduction potential than In, which provides the overall driving force for the CO₂ reduction reaction. Since pure Ga solidifies under ambient conditions (Ga melts at 29.76°C), the incorporation of In was found to be advantageous since it facilitates LM handling at room temperature and avoids unintended solidification of the metal.

The thermal dependence of the formation of carbon was investigated in the decomposition over EGaIn. Based on the kinetic

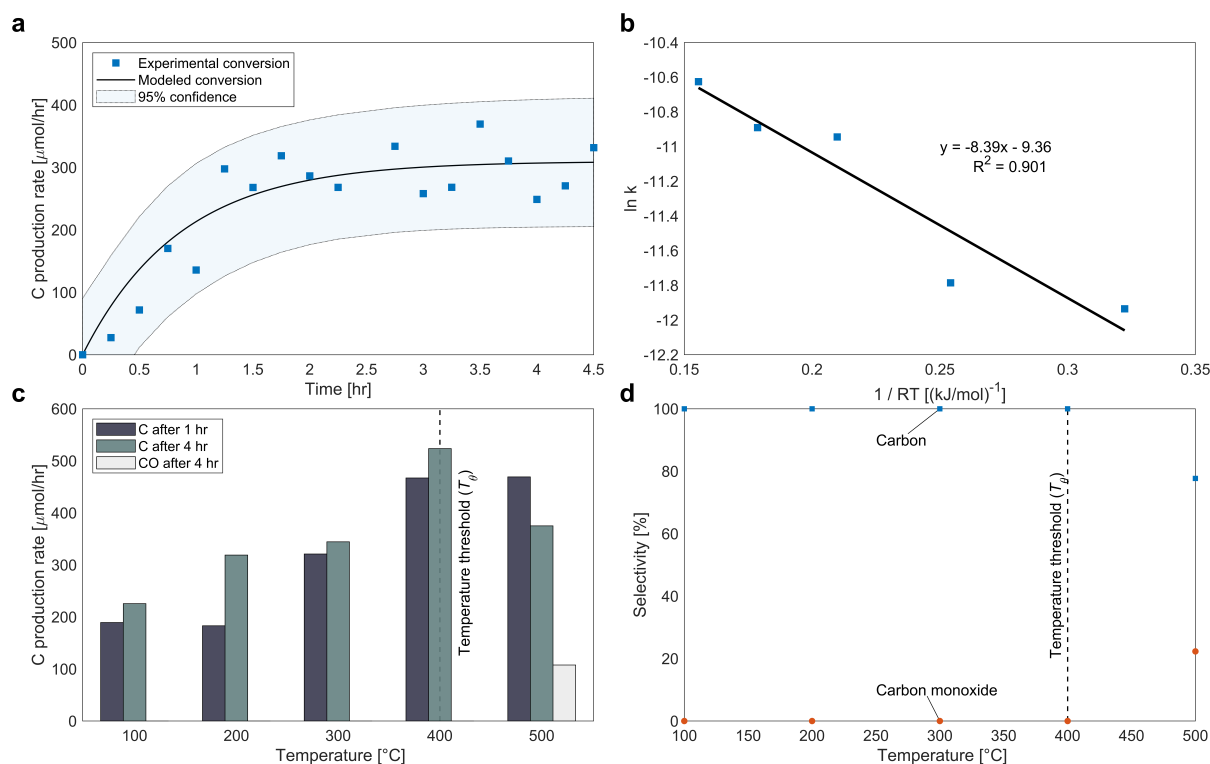


Fig. 2 Performance of the EGaIn alloy. (a) Carbon production rate under continuous flow of CO₂ in a bubbling column reactor, at 200 $^{\circ}\text{C}$ and ambient pressure; (b) Change of logarithmic rate constant with temperature, based on the Arrhenius model, for the empirical determination of the activation energy; (c) Activity of EGaIn at different temperatures under continuous flow of CO₂, showing the Boudouard reaction temperature threshold; (d) Temperature-dependence of the selectivity of EGaIn to carbon and carbon monoxide production after 4hrs reaction.

data, the rate constants (k) were calculated and correlated with temperature through the Arrhenius model (Fig. 2b). As a result, the activation energy for the decomposition of CO₂ to solid carbon over EGaIn was empirically calculated to be 8.39 kJ/mol. Moreover, measurements under continuous flow of CO₂ showed that the steady-state carbon production rate increases with temperature (Fig. 2c). This is further supported in Fig. S4, which highlights a significant increase in the cumulative carbon production after 4 hours of CO₂ decomposition. The stability of EGaIn was evaluated under the same reaction conditions, at 200 $^{\circ}\text{C}$, over a prolonged testing period of 24 hours to assess the change in material properties and activity of the LM (Fig. S5, ESI[†]). EGaIn displayed steady activity, which reflects the thermal stability of these materials in contrast to the rapidly deactivating, continuously reconstructing conventional solid materials.^{24–26} The ensuing implications of the outstanding stability of these LMs exceed preserving the performance of the alloy over the course of the reaction, and extend to attaining recyclable alloys for CO₂ activation.

It was also observed that by operating above a certain temperature threshold (T_{θ}), CO production occurs when CO₂ is in contact with the generated carbon. This can be attributed to the reverse Boudouard reaction ($\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$). As a result, the selectivity to carbon below T_{θ} is maintained at 100%, but tends to decrease above T_{θ} due to the production of CO. The critical temperature T_{θ} was found to be around 400 $^{\circ}\text{C}$. Therefore, to promote

solid carbon formation and to minimize toxic CO production, the LM-enabled dissociation study is restricted to temperatures below 400 $^{\circ}\text{C}$ (Fig. 2d). Experiments at room temperature revealed that EGaIn possesses a remarkable ability to activate and decompose CO₂ to produce carbon (Fig. S2b, Fig. S6 and Fig. S7, ESI[†]), under ambient conditions without the need for an auxiliary source of energy.

To elucidate the mechanism of CO₂ reduction, the surface of EGaIn was examined using in-situ X-ray photoelectron spectroscopy (XPS), with the capability of performing analysis before and after CO₂ exposure without breaking vacuum. XPS measurements of the LM showed that after 30 minutes of exposure to CO₂ the Ga oxide content had increased, whereas In remained metallic (Fig. 3a). The metallic Ga-In ratio at the surface remained constant and no additional alterations to the XPS spectra were observed. The increase in the Ga oxide content is consistent with the findings obtained in LM bubbling column experiments, showing that CO₂ reduction can be achieved using pure liquid Ga. The in-situ operating system replicates the reaction conditions of the bubbling experiment by introducing the CO₂/Ar gas feed at atmospheric pressure and heating the satellite gas reaction chamber to 200 $^{\circ}\text{C}$. Obtaining a pristine metallic surface of the LM is crucial for drawing meaningful comparisons between the surface prior to CO₂ exposure and post CO₂ reduction (see Supplementary note 1, ESI[†]). To that end, the LM was prepared and loaded in a glovebox under nitrogen flow and is transferred into the analysis cell using

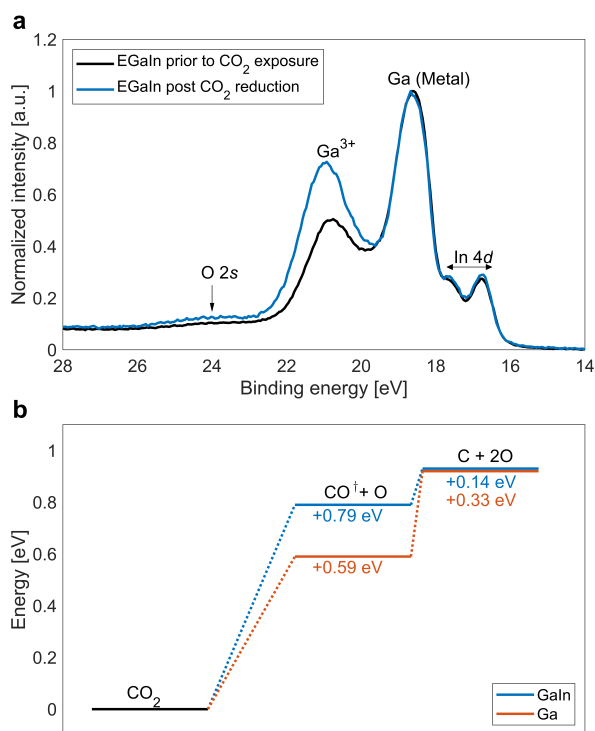


Fig. 3 (a) XPS spectra of the Ga 3d region based on the in-situ assessment of the EGaIn surface before and after 30 mins of exposure to CO₂ at 200°C, showing selective oxidation of the Ga after CO₂ reduction; (b) Reaction energies for the CO₂ dissociation on both Ga and EGaIn slabs.

an air sensitive transporter. Using this loading process, and by maintaining ultra-high vacuum conditions, a pristine metal surface was maintained for analysis pre-CO₂ exposure.

XPS measurements of the LM surface during CO₂ exposure show a 9.6% increase in the carbon-carbon bonding ratio and confirm that no extra carbonaceous species are produced, indicating that pure carbon is the only product of decomposition (Fig. S8, ESI†). Additionally, Raman spectroscopy was employed to analyze the solid carbon product. The relative intensities ($I_D/I_G = 0.295$), and the position of both the disorder induced D band (at 1325 cm⁻¹) and G band (at 1600 cm⁻¹) in the Raman spectrum are characteristic of graphitic carbon (Fig. S9, ESI†). Elemental mapping analysis using energy dispersive X-ray spectroscopy (EDX) of the product obtained post CO₂ decomposition has shown approximately 1:2 carbon to oxygen ratio, and 2:3 gallium to oxygen ratio, reinforcing the stoichiometric decomposition of CO₂ to solid carbon and oxygen, and the consequent formation of gallium oxide (Fig. S10, ESI†). Moreover, EDX was also employed to characterize the separated carbon product, which indicated that the separated product is predominantly carbon, confirming the formation of carbon and gallium oxide in the process (Fig. S11, ESI†). To close the oxidation/reduction cycle of the LM, the gallium oxide produced can be potentially reduced back to gallium using electrochemical reduction methods.²⁷ While the viability of the reduction process is validated through the electrochemical reduction of gallium oxide (see Supplementary note 2 and Fig. S12, ESI†), future work should focus on the regeneration

of the reacted gallium.

Density functional theory (DFT) calculations have been utilized to investigate the adsorption and dissociation behavior of CO₂ on both EGaIn and Ga. The EGaIn alloy was modeled using a slab consisting of 28 Ga atoms and 4 In atoms (Fig. S13, ESI†). The calculations indicate that CO₂ adsorbs on the Ga and In-doped Ga slab surfaces. The CO₂ molecules were found to bind more strongly to a surface Ga atom than to a surface In atom (see Supplementary note 3, Fig. S14 and Fig. S15, ESI†), with the CO₂ aligned almost parallel to the surface. The ability of CO₂ to bind more strongly to a surface Ga atom supports the increase in Ga oxide content obtained from the in-situ XPS measurements. Moreover, CO₂ dissociation energies were calculated for the gas adsorbed on the Ga and Ga-In surfaces (shown in Fig. 3a), which represent the conversion of CO₂ to adsorbed carbon. The dissociation is assumed to occur over two bond breaking stages with each stage representing the cleavage of a C–O bond. For the first oxygen dissociation reaction, a lower reaction energy is determined when using pure a Ga slab (0.59 eV) in comparison to Ga-In slab (0.79 eV). This suggests that there is a lower energy barrier for cleavage of the first C–O bond of CO₂ on the pure Ga slab, according to the Bell-Evans-Polanyi principle.²⁸ However, a lower reaction energy is obtained for oxygen dissociation of the remaining CO molecule on Ga-In (0.14 eV) in comparison to the pure Ga slab (0.33 eV). Therefore, the presence of the In atoms can facilitate the complete dissociation of CO₂ into adsorbed C and O more rapidly. Additionally, bubbling column experiments investigating the reaction under a continuous CO feed were conducted to verify the feasibility of decomposing CO under the same reaction conditions over EGaIn. The measurements indicate that CO decomposes to solid carbon at a steady production rate similar in order of magnitude to that of CO₂ decomposition (Fig. S16, ESI†), supporting the findings of the DFT analysis.

To further elucidate the catalytic mechanism of the EGaIn alloy, Bader partial charges^{29,30} of the CO₂/EGaIn systems were calculated and used to estimate the oxidation state of the Ga and In atoms (see Supplementary note 4, Fig. S17 and Table S1, ESI†). The partial charge of every atom in these systems is reported in Table S2 while Fig. S18 shows the partial charge of selected atoms involved in the CO₂ decomposition reaction.

Prior to adsorption of CO₂ (Fig. S18a, ESI†), the charge in the EGaIn slab (Table S2, ESI†) is delocalized and indicative of bulk-like behavior. The small partial charge of these atoms also corresponds to Ga⁰ and In⁰ species. After adsorption of CO₂ (Fig. S18b, ESI†), there is a redistribution of charge within the substrate and the two O atoms of CO₂ are reduced (by -0.03e each). The small amount of charge transferred from EGaIn to CO₂ (-0.06e) confirms there is a weak interaction that is supported by the relatively weak binding energy (-0.23 eV).

After the first dissociation step (Fig. S18c, ESI†), the free O atom (O1) bonds to two Ga atoms (Ga1 and Ga2) and one In atom (In1) while the CO adsorbs atop Ga4 via O2 and a substantial reduction of the C atom (-1.05e) occurs. Formation of the Ga–O and In–O bonds corresponds to a loss of electrons for Ga1, Ga2 and In1 and suggests a substantial change in their oxidation state (Table S1, ESI†) from Ga⁰ and In⁰ to Ga¹⁺ and In¹⁺. The re-

distribution of charge after this step is also illustrated (Fig. S19c, ESI†) where an accumulation of charge around O1 can be seen concomitant with a depletion closer to the Ga1, Ga2 and In1 atoms. The density of states (DOS) further supports a strong interaction between the adsorbed O atom and both the Ga and In atoms, showing an overlap of the O, Ga and In states between -4.5 to -2 eV (Fig. S20c, ESI†). The adsorbed CO species also withdraws electrons from the surface which results in a substantial reduction of the C atom (-1.05e).

Breaking of the second C–O bond results in coordination of the O2 atom to the Ga5, Ga4 and In1 atoms, and coordination of the C atom to the Ga2, Ga3, Ga4 and Ga6 atoms (Fig. S18d, ESI†). This enhanced coordination results in further charge depletion that is localized around the Ga atoms (Fig. S19d, ESI†) and an increase in the density of states between -4.5 to -3 eV (Fig. S20d, ESI†). For the In1 atom, bonding to both the O1 and O2 atoms results in an increase in charge (+0.64e) and oxidation state (+1.16). Similarly, the adsorption of the O and C atoms to Ga2 and Ga4 atoms results in a significant increase in partial charge (+0.83e and +0.78e), and oxidation state (+1.43 and +1.36) of these two Ga atoms. Overall, decomposition of a single CO₂ molecule on the EGaIn surface leads to an increase in the oxidation state of several top-layer Ga and In atoms that strongly coordinate to the decomposed CO₂ atoms, with their formal oxidation states changing from Ga⁰ and In⁰ to Ga¹⁺ and In¹⁺, respectively.

Conclusion

In summary, we have demonstrated a simple and effective gas-to-solid scheme for the conversion of gaseous CO₂ to solid separable carbon using an LM alloy. Since the requisite for this process is the utilization of metals that are in the liquid phase at the operating temperature, we confined our selection to low melting LMs. EGaIn is liquid at room temperature, making it a great candidate for the low-temperature dissociation of CO₂. In this paper, we have established that EGaIn is consistently effective in decomposing CO₂, enabling the activation of CO₂ at room temperature. Investigations on the thermal dependence of carbon production over EGaIn, revealed that the equilibrium production rate increases with temperature. Based on the in-situ XPS studies and DFT calculations, it can be concluded that Ga is the active component for the decomposition. The process presented in this work can find practical application in decarbonization strategies, making this pathway an integral component of carbon management. Adapting LMs for future CO₂ mitigation catalytic processes will advance the progress toward the production of high-grade functional carbon materials, and the discovery and advancement of next-generation carbon-based materials.

Author Contributions

KZ, TD and KC initiated, designed, and led the work. KZ carried out the experimental work, TD and KC are the academic supervisors who bring different expertise to this project. KZ and AZ performed the product characterization and gallium regeneration experiments. KS helped design the reactor system and analyze kinetic data. KZ and BJM performed the XPS experiments, with

analysis and feedback from BJM and CFM. JCH and MJSS performed and consulted on the DFT calculations. All authors revised and contributed to the final version of the manuscript.

Conflicts of interest

Patent protection is being sought for the invention described in this paper.

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