ACS Energy LETTERS

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Mechanocatalytic Ammonia Synthesis over TiN in Transient Microenvironments

Andrew W. Tricker,[†] Karoline L. Hebisch,[†] Marco Buchmann, Yu-Hsuan Liu, Marcus Rose, Eli Stavitski, Andrew J. Medford, Marta C. Hatzell, and Carsten Sievers*

Cite This: *ACS Energy Lett.* 2020, 5, 3362−3367

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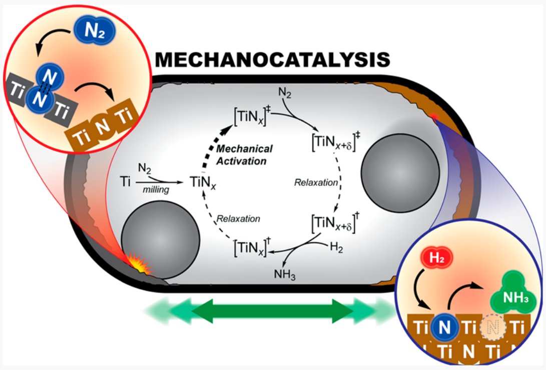
ABSTRACT: Environmentally friendly and energy-efficient ways to produce ammonia are essential to meet global food demands. Here, a new approach for ammonia production at nominally ambient conditions is introduced. As proof of concept, ammonia is synthesized mechanocatalytically by ball milling titanium in a continuous gas flow. The ammonia synthesis reaction is proposed to follow a transient Mars−van Krevelen mechanism under mechanically activated conditions, where molecular nitrogen incorporation into the titanium lattice and titanium nitride hydrogenation occur in thermodynamically distinct environments. X-ray powder diffraction and X-ray absorption spectroscopy confirm the formation of titanium nitride from titanium and N_2. The reactivity of nitrided titanium supports that lattice nitrogen plays a role in ammonia formation. The *in situ* formed titanium nitride is catalytically active, and the nitride regeneration reaction is determined to be the rate-limiting step. A preliminary technoeconomic analysis shows that this approach could be feasible for distributed ammonia production.



The fixation of N_2 to ammonia, a key precursor for fertilizers, is one of the most significant chemical reactions to the modern world,[1,2] fueling the explosive global population growth over the past century. However, ammonia synthesis is burdened by two competing factors: the N_2 triple-bond is very stable (bond energy = 945 kJ mol^{-1}), but ammonia formation is only thermodynamically favored at low temperature. Currently, ammonia is obtained almost exclusively through the Haber−Bosch process, which operates at high temperatures (>400 °C) and pressures (>100 atm) in order to achieve a sufficient rate and conversion.[3] These harsh reaction conditions require specialized facilities and centralized plants, which inhibit local ammonia production in developing regions, restricting access to fertilizers and limiting agricultural output.[4] This process also accounts for ∼2% of global energy consumption and ∼1% of global CO_2 emissions, mainly from hydrogen production via methane reforming.[5,6] New industrial processes that operate under mild conditions, with renewable energy sources, and near end use would facilitate both distributed fertilizer production[7] and a decarbonized ammonia industry.[8] Novel catalytic approaches have utilized electrons,[9,10] photons,[11−13] and nonthermal plasmas,[14,15] as well as looping system conditions,[16−18] to synthesize ammonia closer to ambient conditions. Such processes could produce ammonia directly from nitrogen and water using solar power or operate at scales where water electrolysis is competitive with methane reforming. However, none of these alternative approaches are used industrially, so the need for small scale ammonia synthesis remains unresolved.

Mechanochemistry offers a novel platform for distributed chemical production. Lab-scale applications exist in a plethora of research areas (*e.g.*, organic synthesis,[19−21] materials synthesis,[22,23] heterogeneous catalysis,[24,25] and biomass valorization[26−28]). In these approaches, mechanical energy is applied to the system to drive the reaction, often in ball mills.[29] The energy released during the collisions between grinding balls, reactor walls, and catalyst particles can create transient thermal hot spots,[30] fresh reactive surfaces,[31] and highly active transient defect sites.[32,33] Because of this localized energy input, reactions that traditionally require elevated temperatures and pressures can occur in reactors at nominally ambient conditions. Mechanochemical approaches to chemically bind nitrogen, such as in metal nitrides[34,35] or N-doped

Received: September 2, 2020
Accepted: October 2, 2020

https://dx.doi.org/10.1021/acsenergylett.0c01895

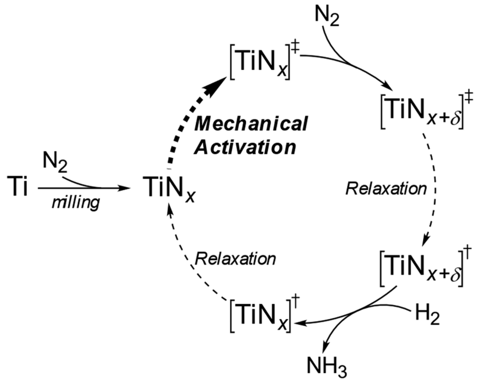
graphite,[36] have been reported. However, mechanocatalytic nitrogen fixation to ammonia has been reported only twice before, more than four decades ago, and over iron-based catalysts.[37,38] Gaps in documentation and analysis make these experiments nonreproducible, and specific understanding of the catalytic reaction and process design were not provided. Therefore, rigorously demonstrating mechanocatalytically synthesized ammonia with modern analytics opens truly new opportunities for distributed ammonia production.

As proof of concept, ammonia was mechanocatalytically synthesized for the first time over an *in situ* formed titanium nitride (TiN) catalyst under nominally ambient conditions (<50 °C, 1 atm) from N_2 and H_2. Milling titanium powder (Ti) in a vibratory ball mill with a stainless steel milling vessel modified to allow a steady gas flow of N_2 and H_2 resulted in the simultaneous formation of TiN and the continuous synthesis of ammonia without the need for external heating or pressurizing.

Ammonia Formation and Proposed Mechanism. Ammonia synthesized by milling Ti in N_2 and H_2 was qualitatively detected by colorimetry (S2.1), mass spectrometry (MS) of the reactor effluent (S2.2), and olfactometry (S2.3), with the possibly of contamination ruled out (*vide infra*). Potential contamination of the Ti with iron (the catalyst of choice for industrial ammonia synthesis) from the steel vessel was considered, but X-ray photoelectron spectroscopy of milled Ti detected no iron (S3.2), and neither iron nor iron oxide showed catalytic activity (Table S1). Finally, synthesizing the catalyst, TiN, from Ti and N_2 in the same system as the ammonia demonstrates catalytic formation from *in situ* fixed N_2 rather than depletion of *ex situ* fixed N_2 in the nitride.

In this mechanocatalytic system, only a small fraction of the catalyst is activated by the ball collision at any given time.[30] The estimated mole fraction of ammonia in the active catalyst void space is 0.06 (S4). In a conventional thermochemical reaction at steady state, this mole fraction would be achievable only up to 230 °C, based on the thermodynamic equilibrium. Notably, collision-induced hot spots are expected to greatly exceed this temperature (e.g., 800 °C during the milling of $CaCO_3$), with the exact number dependent on powder properties.[30,39−41] Additionally, despite nitrides being among the most active catalysts for ammonia synthesis,[42,43] significant thermal catalytic turnovers for TiN were observed only above 600 °C (S5). Thus, a transient Mars-van Krevelen (MvK) process is proposed for mechanocatalytic synthesis (Scheme 1), where N_2 fixation and ammonia formation occur in thermodynamically distinct regimes. TiN is first mechanically activated, forming an environment where N_2 can be dissociated. Next, the TiN relaxes to conditions where ammonia formation is thermodynamically favorable and kinetically feasible, before returning to an inactive state. Parallel reaction pathways may be present, such as through a TiH_2 intermediate, but TiN is expected to be the dominant catalyst (S3.3). This mechanical activation could be a combination of several phenomena (*e.g.*, temperature rise, reactive defect sites and surfaces, and lattice strain). For illustrative purposes, the mechanical activation could be explained by localized heating where the peak temperature enables N_2 activation, but ammonia formation is strongly thermodynamically limited. Analogous to dynamic catalysis,[44] the mechanocatalytic reactor creates a constantly transient reaction environment that increases the local reaction rate by 3 orders of magnitude (S5.2) and circumvents steady-state thermodynamic and kinetic limitations.

Scheme 1. Proposed Transient Mars−van Krevelen Reaction Mechanism for Mechanocatalytic Ammonia Synthesis over Titanium Nitride[a]



[a] Initially, Ti metal is mechanochemically converted into a TiN_x species, which undergoes cyclical mechanical activation and relaxation steps. In the activated states (denoted with † and ‡), the TiN_x acts as a catalyst for ammonia synthesis.

In Situ Synthesis of Titanium Nitride. X-ray Powder Diffraction (XRD) and X-ray absorption spectroscopy (XAS) provided complementary evidence for the mechanochemical synthesis of TiN. XRD showed a substantial change in crystal structure from pure Ti to a Ti/TiN mixture within 1.5 h (Figure 1a). By 3 h, TiN becomes the dominant crystal structure. A peak shift of Ti toward lower diffraction angles has been explained by the formation of a solid solution,[45] with dissolved N atoms expanding the Ti crystal lattice. The peak shift to higher angles of TiN indicates a more compact structure, originating from nonstoichiometric TiN_x phases.[46] The peak broadening and a lower signal-to-noise ratio at increased milling time indicates mechanically induced amorphization.[45,46] Because XRD cannot characterize amorphous phases, XAS measurements of the Ti K-edge were collected. The X-ray absorption near edge structure (XANES) spectrum of Ti milled in N_2 was dominated by characteristic features of TiN (Figure 1b). The Ti pre-edge peak (4965 eV) disappeared; the white line intensity (4895 eV) increased, and the edge shifted by 3.6 eV to a higher energy. The overall XANES line shape is consistent with TiN. The Fourier transform of the EXAFS region (Figure 1c) showed that the Ti milled in N_2 had both a Ti−N shell (1.69 Å) and a Ti−Ti shell (2.52 Å). The smaller radial distance of the Ti−Ti shell in the milled Ti, compared to the TiN, supported the observations of a more compact nitride structure. The diminished intensity is caused by amorphization. Thus, XRD and XAS confirmed the near quantitative *in situ* conversion of Ti to stoichiometric TiN.

Mechanochemical and Mechanocatalytic Ammonia Synthesis Reactions. During the experiment to qualitatively detect ammonia in the reactor effluent with MS (Ti milled in N_2 for 1.5 h then N_2 and H_2 for 6 h), a significant delay of 58 h between the end of milling and the initial detection of ammonia in the gas phase was observed (S2.2). Thus, ammonia yields were measured by washing the catalyst after reaction with deionized water and then performing ion chromatography (IC) with the washing solution (S2.4). Contamination by ambient ammonia is necessary to

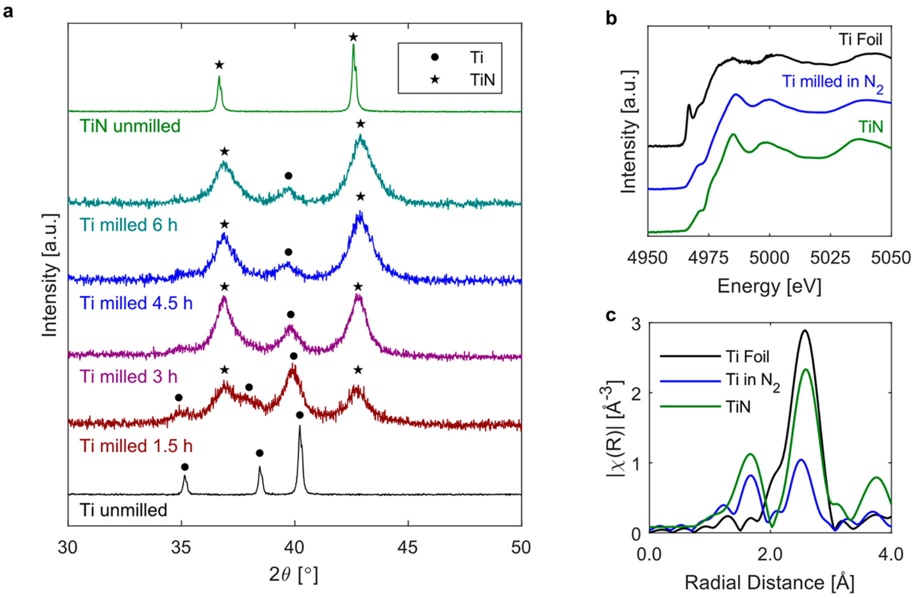


Figure 1. (a) X-ray diffractograms for unmilled Ti, unmilled TiN, and Ti milled for 1.5, 3, 4.5, and 6 h in 15 sccm N_2. Peak assignment was performed according to the unmilled Ti and TiN samples and literature.[47] (b) X-ray absorption spectra of the titanium K-Edge and (c) Fourier transform of the EXAFS region for Ti foil (black), Ti powder milled in N_2 for 4.5 h (blue), and unmilled TiN (green).

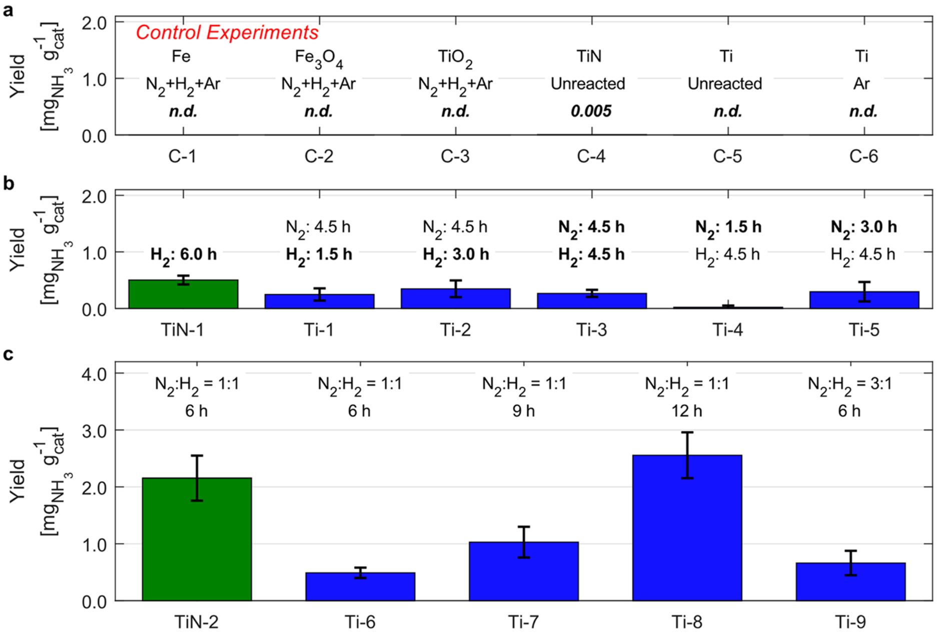


Figure 2. (a) Ammonia yields for control experiments (n.d. = not detected). Full experimental details are reported in Table S1. (b) Ammonia yields for TiN milled in H_2 and Ti milled in N_2 followed by H_2, with varying reaction times. Samples were milled at 30 Hz in a pure gas stream (15 sccm). (c) Ammonia yields for TiN and Ti milled in H_2 and N_2 with varying composition and reaction time. Samples were milled at 30 Hz in a mixed gas flow (15 sccm) of both N_2 and H_2. Full experimental conditions and numeric values are reported in Table S1.

consider.[48−50] Negative results (Figure 2a) from milling iron, iron oxide, and titanium dioxide under reactive conditions ruled out potential contamination in the gas streams, the reactor system, and the IC sample preparation procedure and demonstrate the necessity of the TiN or Ti for positive ammonia detection. Control experiments with TiN and Ti ruled out initial contamination from these materials as well, and background subtraction of initial present ammonia on the catalyst was deemed unnecessary.

The amount of reactive nitrogen in mechanochemical and commercial TiN was studied. Ti samples were first milled in N_2 for 4.5 h, then in H_2 for 1.5, 3, or 4.5 h (Figure 2b, Ti-1—Ti-3). Extending the milling time in H_2 did not significantly increase the ammonia loading. Likewise, milling commercial TiN in H_2 (Figure 2b, TiN-1) and thermally reducing TiN in H_2 (S5.2) resulted in similar ammonia yields. The slightly higher yield from the commercial TiN may arise from incomplete conversion of Ti to TiN during milling. Thus, titanium nitride contains a certain amount of inherently reactive nitrogen, regardless of its synthesis method or reaction environment. After depletion, the residual nitride becomes inactive until replenished with a nitrogen source.

The reactivity of titanium with different nitridation degrees was investigated by milling Ti for 1.5, 3, or 4.5 h in N_2 followed by 4.5 h of milling in H_2 (Figure 2b, Ti-3–Ti-5). Milling for only 1.5 h resulted in background levels of ammonia, while 3 and 4.5 h had yields similar to TiN milled in H_2. This significant increase in ammonia yield by increasing milling time in N_2 from 1.5 to 3 h aligns with the expected nitridation mechanism based on XRD (Figure 1a).[46,47] Initially, nitrogen gradually diffuses into the Ti metal, forming a solid solution. Once a threshold concentration is reached (~32 mol %),[45] a rapid, bulk change to TiN occurs.[46,47] The low ammonia yields at short milling times in N_2 indicate that the dissolved nitrogen is not reactive toward ammonia but must be incorporated into a nitride crystal lattice, supporting a MvK mechanism during catalytic ammonia formation. Thus, a critical amount of incorporated lattice nitrogen is required for relevant ammonia yields.

The catalytic properties of TiN were investigated under steady-state conditions (at a reactor scale as opposed to the spatiotemporally transient conditions at the sites of collisions). Commercial TiN milled in N_2 and H_2 (Figure 2c, TiN-2) showed an ammonia yield four times larger than TiN milled in H_2, indicating that TiN has catalytic activity toward ammonia formation. The ammonia yields from Ti milled in a continuous flow of N_2 and H_2 was measured after 6, 9, and 12 h (Figure 2c, Ti-6–Ti-8). The samples show a continuous production of ammonia by milling, demonstrating that catalytic activity is sustained for an extended period. An induction period can be inferred before catalytic ammonia production starts, which would be expected from the need to first synthesize the TiN. Notably, for both TiN and Ti as (pre)catalyst, significantly higher amounts of ammonia are achieved under continuous conditions, compared to the experiments with a separate feed (Figure 2b). Thus, the presence of N_2 in the feed allows for continuous nitride regeneration, and this regeneration ability is sustained for extended times via a fully catalytic process.

The influence of feed composition and nitride content are two key parameters that will control the catalytic behavior of the system. Two Ti samples (Figure 2c, Ti-6 and Ti-9) were milled in different gas compositions, 1:1 and 3:1 N_2:H_2, respectively. The influence of gas composition and nitride content cannot be completely separated as milling Ti in a mixture of N_2 and H_2 results in a mixture of nitride and hydride phases (S3.3). However, the nitride to hydride ratio increased with higher N_2 content in the gas phase. The 50% increase of N_2 in the gas phase did show an increase in ammonia yield, though precise discussion is difficult because of the large error bars between Ti-6 and Ti-9. Obtaining higher ammonia yields with a higher N_2 feed and greater nitride content suggests that the ammonia synthesis rate is limited by the nitride regeneration rate. Optimal catalytic activity is expected to require a balance of stability of the nitride, with a more stable nitride than TiN exhibiting higher activity due to greater nitrogen binding and nitride formation energies. By further studying these parameters and more traditional thermal nitride catalysts (*e.g.* MoN[51,52] and Co_3Mo_3N[42,53]), higher mechanocatalytic ammonia yields should be obtained.

Preliminary Technoeconomic Analysis. When introducing a new approach, addressing the feasibility of the process is valuable to frame its broader significance. Metrics laid out by Comer et al. suggests preliminary performance targets for solar-powered fertilizer processes of 8.83×10^4 kJ $\mathrm{mol_N}^{-1}$ energy consumption and 100 $\mathrm{kg_N}$ $\mathrm{ha^{-1}}$ $\mathrm{yr^{-1}}$ production rate.[7] Other novel approaches for distributed fertilizers (i.e., electrocatalysis, photocatalysis, and plasma-assisted catalysis) produce ammonia at energy consumptions of 10^4–10^5 kJ $\mathrm{mol_N}^{-1}$.[7] A small, electric industrial ball mill (1 m^3) would have a typical mineral (i.e., catalyst) loading of 10^3 kg while requiring 10^4 W to operate.[54] A preliminary technoeconomic analysis (S6) shows that ammonia could be produced at 10^3 kg yr^{-1} with a solar energy consumption of 10^4 kJ $\mathrm{mol_N}^{-1}$ (assuming 20% solar panel efficiency). Such a mill could produce fixed nitrogen equivalent to the necessary amount to fertilize a small to medium sized farm (~10 ha) and be powered onsite with the typical output of 200 solar panels.[7] Future assessments would need to account for nitrogen separation from air, hydrogen production via electrolysis, and upgrading the ammonia to fertilizers (e.g., urea or ammonium nitrate). Notably, mechanocatalysis has unique advantages, such as generating catalysts *in situ* from abundant materials and utilizing nonelectrical sources of renewable energy (i.e., direct mechanical energy from wind or water mills). While this assessment is preliminary, it reveals that mechanocatalysis is clearly competitive with other well-studied alternative systems for distributed ammonia production.

In summary, a novel approach to ambient ammonia synthesis via mechanocatalysis is introduced, where N_2 and H_2 are catalytically reacted over an *in situ* synthesized nitride catalyst. By creating transient microenvironments, kinetic and thermodynamic limitations are elegantly circumvented. A transient Mars–van Krevelen mechanism is proposed, comprising nitrogen incorporation and titanium nitride hydrogenation steps. The catalytic cycle is rate limited by the nitride regeneration, thus a more stable nitride is expected to yield higher ammonia rates.

This work demonstrates how mechanocatalysis provides fundamentally new opportunities to exploit spatiotemporal variations in thermodynamic driving forces and kinetic phenomena to make difficult chemistry accessible at benign conditions. The mechanocatalytic process shown here could foreseeably be utilized for other reactions with similar kinetic and thermodynamic mismatches, such as the partial oxidation of methane to methanol[55,56] or the water gas shift reaction,[57] opening new avenues for distributed chemical production.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c01895.

Detailed experimental methods, ammonia detection figures and data, thermodynamic calculations, additional catalyst characterization figures, and preliminary technoeconomic calculations (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Carsten Sievers – *School of Chemical & Biomolecular Engineering and Renewable Bioproducts Institute, Georgia Institute of Technology, Atlanta, Georgia 30332, United States;* orcid.org/0000-0002-5713-1875; Phone: (404) 385-7685; Email: carsten.sievers@chbe.gatech.edu

Authors

Andrew W. Tricker − *School of Chemical & Biomolecular Engineering and Renewable Bioproducts Institute, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*
Karoline L. Hebisch − *School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*
Marco Buchmann − *Department of Chemistry, Technical University of Darmstadt, 64287 Darmstadt, Germany*
Yu-Hsuan Liu − *School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*
Marcus Rose − *Department of Chemistry, Technical University of Darmstadt, 64287 Darmstadt, Germany;* orcid.org/0000-0001-8196-1353
Eli Stavitski − *National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States*
Andrew J. Medford − *School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*
Marta C. Hatzell − *The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*

Complete contact information is available at:
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Author Contributions

[†]A.W.T. and K.L.H. contributed equally. M.C.H., A.J.M., and C.S. proposed the idea behind the research. A.W.T. and K.L.H. designed the experiments. C.S. supervised the project. Y.-H.L. helped with ion chromatography. M.B. and M.R. designed and performed the thermal ammonia experiments. E.S. supervised and conducted the XAS experiments and analysis. K.L.H. performed material characterization. A.W.T. performed the technoeconomic analysis. A.W.T. and K.L.H. conceptualized the Letter and wrote the original draft of the manuscript. All authors discussed the results and reviewed and edited the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Dr. Laura da Silva for her contribution in initial catalyst-screening experiments. The authors also thank Dr. David Tavakoli and Walter Henderson for assistance with and discussions of the XRD experiments. A.W.T. acknowledges support from a PSE fellowship from the Renewable Bioproducts Institute at the Georgia Institute of Technology. K.L.H. thanks the Bundesministerium für Bildung und Forschung (German Federal Ministry of Education and Research) and BASF SE for their support by the Deutschlandstipendium. M.C.H. and Y.-H.L. acknowledge that this material is based upon work supported by the National Science Foundation under Grant No. 1846611. M.R. and M.B. acknowledge financial support by the German Research Foundation (Grant No. RO 4757/5-1). This research used resources of the beamline 8-ID ISS (Inner Shell Spectroscopy) in the National Synchrotron Light Source II and the Center for Functional Nanomaterials, which are U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704. The XRD work was performed in part at the Materials Characterization Facility (MCF) at Georgia Institute of Technology. The MCF is jointly supported by the GT Institute for Materials (IMat) and the Institute for Electronics and Nanotechnology (IEN), which is a member of the National Nanotechnology Coordinated Infrastructure supported by the National Science Foundation (Grant ECCS-1542174).

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