

High-Conversion Propane Dehydrogenation by Photocatalysis under Ambient Conditions

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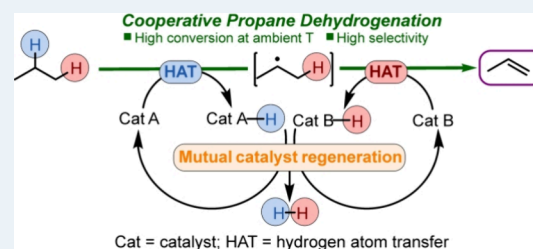
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ABSTRACT: Propane dehydrogenation has been actively pursued as a promising method for propylene production to fill a growing supply–demand gap. Limited by the thermodynamics of this transformation, existing approaches face challenges of relatively low conversion and the need for a high temperature and low pressure. In this work, we report a photocatalytic approach that enables conversion beyond what can be achieved by conventional thermocatalysis. With sodium decatungstate and cobaloxime pyridine chloride as cooperative photocatalysts, we achieved a benchmark in propane dehydrogenation of 68.9% conversion and near-unity selectivity toward propylene production at room temperature and atmospheric pressure with hydrogen as the only byproduct. These results prove the concept of dehydrogenating propane for propylene production using light as the key energy input.

KEYWORDS: photocatalysis, propane dehydrogenation, ambient conditions, hydrogen atom transfer, cooperative catalysis



INTRODUCTION

Propylene, as an important feeding stock for the synthesis of commodity chemicals such as polypropylene and acrylonitrile, faces a growing global supply–demand gap.¹ Among its production methods, propane dehydrogenation (PDH) promises an on-purpose route that holds great potential to bridge the gap, benefiting from not only the abundance of propane supplies thanks to the shale gas boom but also the high selectivity of propane to propylene conversion.^{2–4} For these reasons, PDH has attracted significant research attention.^{5–11} The thermodynamic limit of this process is recognized as a key factor that limits its further development. For instance, as an endothermic reaction, a higher yield of propylene is expected at higher temperatures; however, raising the temperature also compromises the selectivity and catalyst durability.^{1,12} Consequently, most PDH is operated at temperatures ranging from 550 to 620 °C (Figure S1 and Table S1).^{13–28} The second parameter that has significant implications for PDH is pressure. As an entropy-increasing reaction, the production of propylene is favored at low partial propane pressures, which is achieved by diluting the reactant with inert gases; however, doing so decreases the overall yield of the product and incurs additional separation costs. Presently, the state-of-the-art benchmark of PDH at atmospheric pressure features a ca. 40% conversion at a temperature of 580 °C (Figure S1).¹⁴ In principle, this limit could be readily broken with the addition of oxidants to change the product of H₂ to H₂O, transforming the overall reaction to exothermic.²⁹ The most direct benefit of this approach would be greatly reduced operating temperatures. Indeed, efforts have

been undertaken to exploit oxidative PDH for propylene production.^{30–34} Nevertheless, low product selectivity and possible safety concerns are issues that require further research to resolve. Taken together, for practical applications, high conversion of propane to propylene at low temperatures and high pressures is desired but remains elusive. Here, we report a fundamentally different approach to meeting this challenge. We demonstrate high conversion of PDH under ambient conditions (room temperature and 1 atm pressure) through photocatalysis. A new benchmark of 68.9% conversion and near-unity selectivity to propylene is achieved (Figure S1), opening up new pathways to this important transformation.

RESULTS AND DISCUSSION

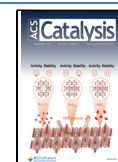
Different from the existing PDH processes, our strategy involves two distinctly different catalysts through a cooperative mechanism. As shown in Figure 1, the first catalyst, sodium decatungstate (Na₄[W₁₀O₃₂], NaDT, where DT refers to the decatungstate anion) is effective in activating the C–H bond and abstracting one hydrogen atom upon photoexcitation, producing a propyl radical (see trapping experiments in the Supporting Information (SI)). The intermediate is then further activated by the second catalyst, cobaloxime pyridine chloride

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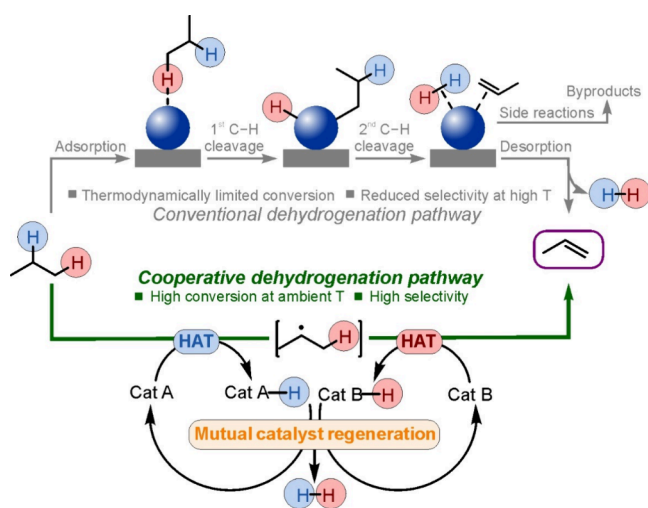


Figure 1. Comparison of dehydrogenation pathways by traditional thermocatalysts (top) and cooperative photocatalysts (bottom).

(COPC), to abstract a second hydrogen in the α position, leading to the formation of propylene. The reduced DT and oxidized COPC finally react with each other to release H_2 and regenerate both catalysts. The net overall reaction is PDH, with the production of propylene and H_2 . In a typical experiment, 1 atm of propane was introduced into a vacuumed reactor (85 mL) containing 3 mol % NaDT, 3 mol % COPC, and 6 mol % dimethylglyoxime (ligand, $dmgH_2$) dissolved in 40 mL of acetonitrile. The resulting mixture underwent irradiation with 485 mW/cm^2 of 365 nm LED light for 20 h at 22°C (all molar percentages are relative to propane; see the

SI for experimental details and reaction setup, Figure S2). A conversion of 60.0% with >99% selectivity to propylene was observed, along with H_2 gas generation at a 1:1 ratio to propylene. The conversion could be further increased to 68.9% when fresh COPC was added after a 20 h course of reaction, and the reaction was continued for another 20 h (Figure S1, vide infra). When compared with existing reports on PDH, the performance achieved here represents a major advancement toward low-temperature, high-pressure, and high-conversion applications. The key enabling factor is our choice of catalysts, which are hydrogen atom transfer (HAT) catalysts that are photoactive.³⁵ They allowed us to perform the reaction at room temperature. Nevertheless, the catalyst we have chosen (NaDT), while highly active to abstract H from C_3H_8 , is difficult to regenerate. By comparison, the second catalyst, COPC, is much weaker in activity toward hydrogen atom abstraction (HAA) and, as a result, is active only in reacting with the propyl radical intermediates. However, the resulting cobalt hydride equivalent species is highly effective in regenerating reduced DT and thus completing the full catalytic cycle.^{36,37} Together, they work cooperatively to achieve PDH with a minimum byproduct formation.

Our strategy of utilizing DT as a HAT photocatalyst is inspired by prior reports that demonstrated the functionalization of light alkanes including isobutane, propane, ethane, and methane with DT.^{38,39} These pioneering works had to trap the radical intermediates after HAA by photoexcited DT with acceptors, whereas the reduced DT ($H^+[W_{10}O_{32}]^{5-}$) was regenerated during the H back-donation process.³⁸ In the context of PDH, there are no such acceptors to regenerate the reduced DT, which presents a challenge. This issue was partially solved by Sorensen and co-workers with the

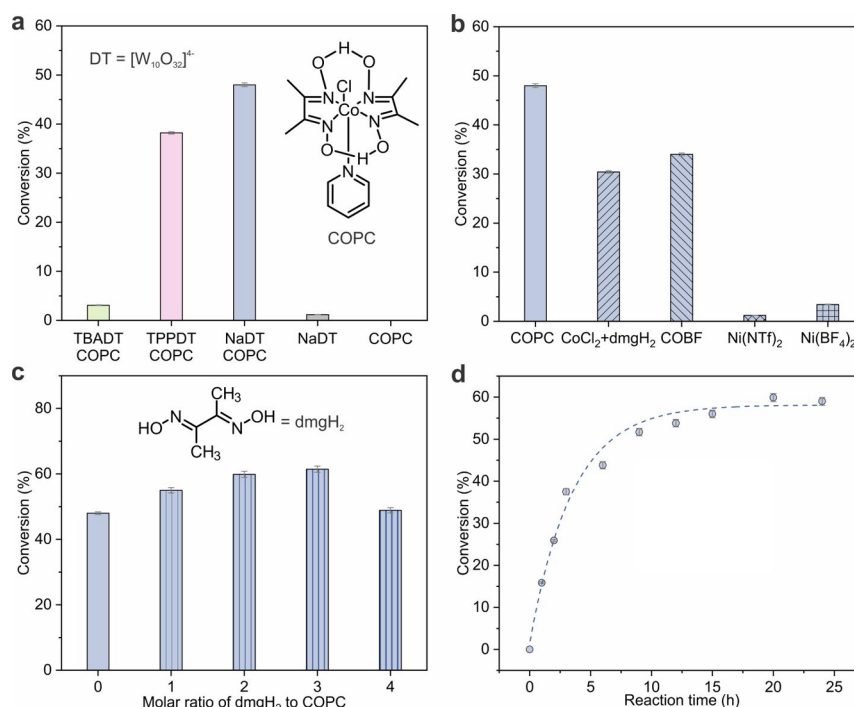


Figure 2. All reactions in panels (a–c) were conducted in the presence of 1 atm of propane in an 85 mL high-pressure vessel with 3 mol % of each catalyst dissolved in 40 mL of acetonitrile at 22°C for 20 h with an irradiation of 485 mW/cm^2 of 365 nm LED. (a) Comparison of the photocatalyst with different cations. (b) Comparison of different cocatalysts. (c) Comparison of different ligand concentrations as a strategy to stabilize COPC as a cocatalyst. (d) Time-dependent PDH conversion rate with 3 mol % NaDT, 3 mol % COPC, and 6 mol % $dmgH_2$. Error bars represent the standard deviations of at least three independent experiments conducted under the same conditions.

introduction of a second catalyst, COPC, in their prototypical demonstration of cycloalkane dehydrogenation.⁴⁰ The catalytic system was then elaborated by the Sorensen and Wendlandt groups in other types of reactions.^{41–45} Notwithstanding, cooperative catalysis for dehydrogenation has not been applied to light alkanes such as propane, to the best of our knowledge. Given the importance of PDH, we are motivated to build on existing knowledge and enable PDH with photocatalytic dehydrogenation. In implementing this idea, we first encountered issues with the popularly used cations in DT-based photocatalytic studies, tetrabutylammonium (TBA). It was found that photoexcited DT was active toward HAT from TBA, producing but-1-ene and leading to catalyst deactivation (Figure S3). More broadly, the observation raised concerns over using cations with functional groups that contain aliphatic C–H bonds in DT-based catalysis.⁴⁶ To support this hypothesis and address this concern, we replaced TBA with tetraphenylphosphonium (TPP), a similar organic cation but without aliphatic H. As expected, a significantly increased conversion of up to 38.2% was achieved because of the improved catalyst durability and, consequently, greater catalyst turnovers (Figures 2a and S4–S6). Given the large size of TPP and thus possible steric hindrance that may limit the reaction between DT and propane, we next tested a much smaller cation, Na⁺ (Figures 2a and S4).⁴⁷ To our satisfaction, an improved conversion (48.0%) was readily measured. Consequently, for the rest of this work, we employed NaDT as the photocatalyst to abstract the first H atom from propane.

The second question we sought to answer was the necessity of the second catalyst, COPC. In our initial attempt to perform PDH, only NaDT was used. In a typical experiment that involved 3 mol % NaDT, ca. 1.2% conversion of propane to propylene was measured, but no H₂ was detected. The result suggested that while effective in abstracting the H atom from propane, NaDT was not turned over, and the propylene formation was stoichiometric to DT reduction. How to turn over H⁺[W₁₀O₃₂]⁵⁻ thus became a critical issue that must be addressed. Inspired by our parallel efforts to use DT for the depolymerization of native lignin, we proposed that the regeneration of DT may be achieved by adding oxidants.⁴⁸ For this purpose, we added sodium persulfate (Na₂S₂O₈) as an electron scavenger but only observed a modest increase in the conversion (to 1.5%), whereas the introduction of molecular oxygen exhibited adverse effects on the reaction (Figure S7).⁴⁹ We next studied COPC as a second HAT catalyst.⁴⁰ The advantages offered by COPC are 2-fold. First, as a mild HAT catalyst, it is not expected to compete with DT in activating propane, which otherwise would undermine the effectiveness of DT and consume COPC. Instead, COPC only reacts with the propyl radical as the product of the DT HAA of propane. Indeed, no products were detected when COPC was employed as the sole catalyst. Second, and more importantly, the product of HAA by COPC is a hydride equivalent that readily reacts with H⁺[W₁₀O₃₂]⁵⁻ to release H₂ and regenerate both catalysts.^{40,50} Such an expectation was indeed supported by the detection of a stoichiometric amount of H₂ relative to propylene. Cooperatively, a catalytic cycle, as shown in Figures 1 and S8, is complete. In examining the catalyst mechanism, one more question deserves additional consideration. That is, does DT compete with COPC in abstracting H from the propyl radical intermediate? Our working hypothesis is that the competing reaction between COPC and propyl radical is favored. This is not only because the radical (electron-

withdrawing) disfavors interactions with activated DT (an electrophile), which is present in low concentrations, but also due to the expected lower concentrations of the propyl radical as an intermediate than propane as a reactant. Combined, photoactivated DT predominantly abstracts the H atom from propane. The net result is that photoactivated DT abstracts the first H from propane and COPC abstracts the second H, producing propylene and H₂ in a cooperative manner.

As proposed in Figure S8, the second HAT proceeds by trapping the propyl radical with the cobalt center, followed by β -H elimination. We studied similar catalysts previously reported for their ability in β -H elimination (Figure 2b).^{51–53} While other cobalt-based catalysts, including in situ-generated [Co(dmgH)₂] species (formed by combining cobalt salt with dmgH₂) and N,N',N'',N'''-(tetrafluorodiborato)bis[μ -(2,3-butanedionedioxiato)]-cobalt(II) dihydrate (Co(dmgBF₂)₂(H₂O)₂, COBF), exhibited substantial conversions for PDH, they were less effective than COPC. Similarly, nickel-based catalysts, such as nickel(II) trifluoromethanesulfonate (Ni(Tf)₂) and nickel(II) tetrafluoroborate hexahydrate (Ni(BF₄)₂·6H₂O), were even less effective. These results highlighted the effectiveness of the NaDT and COPC dyad as cooperative photocatalysts for PDH. Of the dyad, DT has been demonstrated to be stable and recyclable,⁵⁴ but COPC was previously reported to be more prone to degradation, possibly due to hydride transfer from the Co metal center to the ligand.^{55,56} We therefore hypothesized that its durability was a limiting factor. To test this understanding and further increase the conversion, we introduced an additional ligand dmgH₂ to stabilize COPC because the catalytically active cobaloxime species [Co(dmgH)₂] could be generated in situ with leached Co salts due to ligand degradations.^{51,57,58} As shown in Figure 2c, this addition of a ligand in fact enhanced PDH conversion, increasing it from 48.0 to 60.0% with the addition of 6 mol % dmgH₂. When the addition was increased to 9 mol %, the conversion was further improved to 61.4%. Beyond this, however, a lower conversion was measured with more dmgH₂, presumably due to side reactions such as hydrogenation of the ligand itself.⁵⁹ For subsequent experiments, 6 mol % dmgH₂ was chosen as a typical additive. Next, we performed a time-dependent analysis of PDH conversion using optimized catalyst combinations (3 mol % NaDT, 3 mol % COPC, and 6 mol % dmgH₂). It is apparent that the reaction proceeded rapidly initially but slowed down significantly after 6 h and eventually stalled after 20 h (Figure 2d). As such, a reaction time of 20 h was selected as a typical reaction duration. It is important to note that in all control experiments discussed above, no measurable byproducts involving propane were detected, highlighting the excellent selectivity of the photocatalysts in PDH. As a preliminary test of its utility beyond PDH, we also applied the same catalyst system to ethane dehydrogenation (EDH), the most thermodynamically challenging dehydrogenation reaction,⁶⁰ and obtained a conversion of 26.8% and >99% ethylene selectivity under standard reaction conditions. The results are remarkable, and there should be plenty of room for further optimizations.^{4,61,62}

To shed more light on the working mechanism of the catalytic system, we next performed kinetic studies by varying four key factors: light intensity, propane pressure, NaDT concentration, and COPC concentration (Figure 3). For this set of experiments, we limited the reaction time to 3 h to rule out possible complications such as mass transport limitations

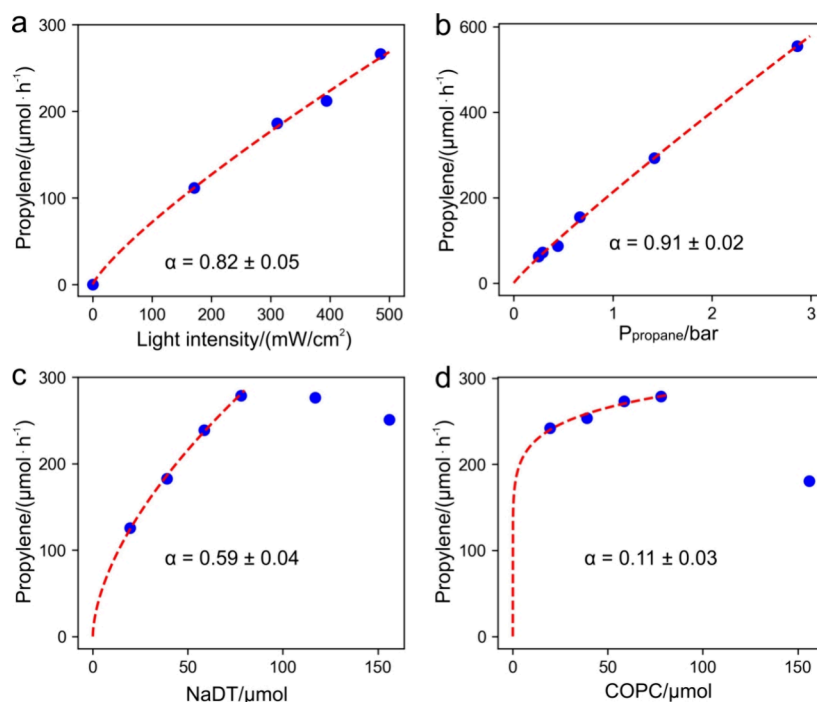


Figure 3. Kinetic studies of photocatalytic PDH. The reaction rate dependence on (a) light intensity (170–485 mW/cm²), (b) propane pressure (0.25–4.23 bar), (c) NaDT concentration (20–156 μmol), and (d) COPC concentration (20–156 μmol, with 40–312 μmol of dmgH₂). The data were fitted by using the rate equation $r = k[A]^\alpha$, where α represents the apparent reaction order of each variable. Plots with log–log fitting and derived function fitting are available in the SI.

in prolonged reactions. As shown in Figure 3a,b, a pseudo-first-order dependence of the reaction rate on light intensity and propane pressure was observed, supporting that the activation of propane by photoexcited DT is a kinetic limiting factor. Consistent with this observation is the weak dependence of the reaction rate on the COPC concentration (Figure 3d). Similarly, the dependence of the reaction rate on DT concentration was also relatively weak, implying the availability of DT is less important than its photoexcitation. This understanding is further supported by the apparent decrease of the reaction rate when higher concentration DT or COPC was used, presumably due to the quenching effect of cobaloxime to the singlet excited state of DT and/or the competitive light absorption between ground-state DT and the Co-species involving the β -H elimination process.^{51,63} Lastly, the reaction rate was the highest when the molar ratio of NaDT and COPC was 1:1, further supporting the cooperative behavior of the two catalysts.

To gain deeper insights into the cooperative photocatalytic process within our system, we next conducted density functional theory (DFT) calculations on the catalytic cycle (Figure 4, see the detailed computational methods in the SI). The first HAT processes, involving the generation of reactive DT species under light excitation and the subsequent HAT of propane to form propyl radicals, are thermodynamically favorable, releasing free energies of 0.92 and 0.27 eV, respectively. This aligns well with our observation of the highest-order dependency of the reaction rate on propane pressure (Figure 3b). The subsequent trapping of the resulting propyl radicals by cobaloxime(II) species is also energetically favorable. However, the β -H elimination process necessitates a free energy of 0.47 eV to proceed, which could be easily overcome by light energy, supporting our hypothesis and previous findings suggesting that this step is driven by

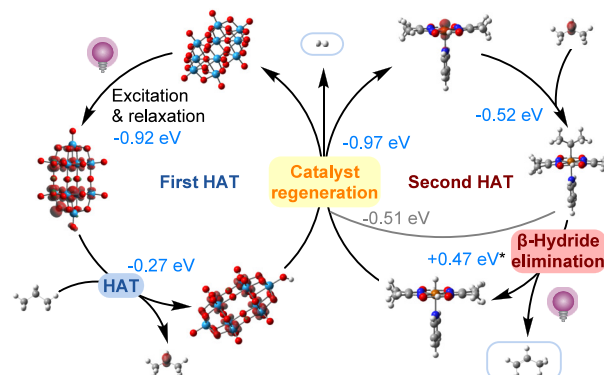


Figure 4. DFT calculation of the cooperative catalytic cycle. The numbers are the free energies for each step. Color code: cyan, W; red, O; gray, C; white, H; blue, N. *This energy is without consideration of light energy. Note that n-propyl radicals were also generated but much less favorably (see details in the trapping experiments in the SI). For simplicity, only isopropyl radicals were considered in the calculations shown here.

photolysis.^{51,63} Our observations further correlate with the conversion rate achieved when NaDT and COPC are in a 1:1 molar ratio. Nevertheless, at the current stage, we cannot discount the possibility that the second HAT event occurs via direct abstraction of the propyl radical by cobaloxime, as proposed by Sorensen,⁴⁰ or via direct β -H abstraction by reduced DT species, leading to the release of H₂ and C₃H₆ and the regeneration of cocatalysts, a process that is energetically favorable.

According to our calculation results, all reaction steps are energetically favorable under our reaction conditions, indicating that achieving high PDH conversion is feasible. While experimentally achieving a conversion of 61.4% under ambient

conditions is remarkable for PDH, it would be interesting to ask how this figure of merit can be further improved. We hypothesize that catalyst deactivation, especially that of the COPC, is the main limiting factor. This understanding was supported by characterizations of the spent solution by proton nuclear magnetic resonance spectroscopy (^1H NMR, Figure S9). Further supporting evidence was that additions of fresh COPC pushed the PDH conversion up to 68.9% (Figure S1). Attempts to further increase the conversion were unfruitful, possibly due to contamination effects by deactivated catalysts in the reaction system. To learn more about the conversion limit, we performed control experiments by premixing propylene and H_2 gases at a 1:1 pressure ratio with varying amounts of propane to mimic the end of a hypothetical reaction and then added fresh catalysts to observe whether there was additional conversion of propane to propylene. Our goal was to experimentally test whether there is a limit to the conversion. For a mixture starting with 63.5% propylene, its concentration could be pushed to 81.6% after a 20 h reaction; this value could be further pushed to 94.8% propylene with a starting concentration of 90.9% (Figure S10). These results strongly suggest that aside from catalyst durability, there appear to be no other apparent limiting factors. Higher practical conversion than reported here is possible with process engineering, such as pursuing flow-type reactors.

It is nevertheless important to acknowledge both the promises and challenges for the practical implementation of photocatalytic PDH. For instance, in the current proof-of-concept demonstration, UV light is needed, which could raise concerns about the prospect of direct sunlight utilization. There are two primary strategies for utilizing solar energy in photocatalysis: direct utilization of solar light with panel reactors or conversion of solar energy to electricity followed by generating light with LEDs as artificial solar light. Both large-scale and commercialized reactors are emerging in these directions.^{64–66} Although the current catalytic system outperforms previously reported photocatalytic systems in terms of conversion efficiency, selectivity, and reaction rate (space-time yield) (Table S2), the reaction rate in our current system is not yet fully optimized (see Table S1 for comparison). The relatively slow reaction rate may be due to the gas–liquid reaction nature of the system, where mass transfer from the gas phase to the liquid phase could retard the process. We also recognize the crucial importance of catalyst stability and recyclability for practical applications. Efforts are underway in our laboratory to explore catalyst immobilization and confinement, as well as flow reaction setups. These considerations notwithstanding, the findings reported here serve as inspirations for further research on PDH that features high conversion and outstanding selectivity.

CONCLUSIONS

In conclusion, we successfully demonstrated PDH at room temperature and ambient pressure, achieving a high conversion of 68.9% with the assistance of photocatalysis. This performance not only establishes a new benchmark in the field but also validates our hypothesis that remarkable selectivity can be achieved by employing HAT catalysts specifically designed for C–H bond activation. Furthermore, our results have proven the concept that with the aid of photocatalysis, PDH has the potential to achieve nearly complete conversion, addressing a long-standing challenge in thermocatalytic PDH methods and opening a new path for PDH. Additionally, this strategy can be

easily applied to the most thermodynamically challenging EDH, producing a striking conversion of 26.9% and near-unity selectivity, indicating the general applicability of the strategy for light alkane dehydrogenation.

METHODS

Procedures for PDH Reactions. Catalytic PDH reactions were conducted in a glass pressure reaction vessel (3 oz, ca. 85 mL in total volume) purchased from Andrews Glass with customized Swagelok reactor tops. The reaction setup is shown in Figure S2. In a typical PDH experiment, 191 mg of NaDT was first dissolved in 30 mL of acetonitrile at 90 °C. After complete dissolution, the solution was cooled down to room temperature, then 32 mg of COPC and 18 mg of dmgH_2 were added to the solution, and 10 mL of acetonitrile was further added to flush the chemicals adhered to the vessel wall into the solution. Then the reactor was sealed by the modified Swagelok reactor top with a needle-valve adaptor and an O-ring. Grease was also applied at the edge of the reactor to ensure the airtightness of the reaction system. The air inside the vessel, which was dissolved in the solution, was removed with a freeze–pump–thaw technique three times in the dry ice/acetone bath in a cryogenic storage dewar. Afterward, the vessel was filled with 1 atm propane and was irradiated by a 365 nm LED (Howsuper, H6015-S-6868-LG-365 nm) stirring at 700 rpm. The reaction temperature was maintained at ca. 22 °C in a water bath in a jacketed beaker that was connected to a water-cooled chiller.

For the PDH experiments starting with premixed gases of propane, propylene, and hydrogen, a gas stock was first mixed by charging propane, propylene, and hydrogen in a certain ratio (indicated by the gauge on the reactor) to a total pressure of >10 bar into an empty reactor. Then, this gas stock was used as the starting gas for the reaction; typically 4 bar of mixed gases was used for each reaction. The conversion of propane in these experiments was obtained by directly comparing the gas amounts after the reaction with those of the mixed gases in the same setup but without LED irradiation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c06192>.

Materials and reagents; synthesis of DT catalysts, measurements of products; trapping experiments; computational methods; picture of the experimental setup; ^1H NMR spectra obtained using the TBADT/COPC system; UV–vis spectra of NaDT and TPPDT; typical GC chromatogram obtained after a PDH reaction; measurements of K_{H} of propane and propylene in acetonitrile; oxidative PDH with NaDT and different oxidants; unfavorable transition state illustrating the poor performance with the oxidative PDH pathway; proposed mechanism; ^1H NMR spectra of fresh and spent COPC; reactions of the premixed gas mixture; and summary of the catalytic data of PDH catalysts (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y.Y. and Y.Z. contributed equally.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PDH, propane dehydrogenation; NaDT, sodium decatungstate; COPC, cobaloxime pyridine chloride; dmgH₂, dimethylglyoxime; HAT, hydrogen atom transfer; HAA, hydrogen atom abstraction; TBA, tetrabutylammonium; TPP, tetraphenylphosphonium; COBF, N,N',N'',N'''-(tetrafluorodiborato)-bis[μ-(2,3-butanedionedioximato)]cobalt(II) dihydrate; EDH, ethane dehydrogenation; ¹H NMR, proton nuclear magnetic resonance; DFT, density functional theory

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