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Photoelectrochemical iron–cobalt synergistic catalysis for C(sp^3)–H alkenylation†

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Electrocatalysis and photocatalysis have both emerged as increasingly feasible platforms in sustainable synthesis. This study explores a novel photoelectrochemical synergistic strategy, achieving non-directed C(sp^3)–H alkenylation reaction utilizing an iron–cobalt dual catalytic system. With the synergy of photoelectrochemical redox catalysis and iron–cobalt catalysis, efficient C(sp^3)–H alkenylation reaction of alkanes as well as dehydrogenation occur without the need for chemical oxidants or reductants, yielding hydrogen gas as the sole byproduct. The electric current is employed to modulate the oxidation states of the catalysts, fulfilling a role similar to that of external oxidants typically used in transition metal catalysis. This method demonstrates unconventional regioselectivity, with a preference for alkenylation at the 1° C–H bonds. This research not only demonstrates that alkenes as radical acceptors can influence the regioselectivity but also offers a promising pathway for advancing iron-catalyzed C–H functionalization.

Introduction

Alkane resources are abundant and cost-effective, widely present in natural gas and associated with petroleum. However, despite their abundant reserves, only a small portion is converted into high-value chemical products. It is crucial to sensibly utilize fossil resources such as petroleum and natural gas.[1] The functionalization of inert alkanes poses a significant challenge due to the high bond energy of C–H bonds.[2] To achieve meaningful transformations, an increasing variety of hydrogen abstractors have been developed, including eosin Y,[3] diaryl ketones,[4] and decatungstate.[5] Recent years have witnessed remarkable advancements in transition metal-catalyzed reactions leveraging visible light irradiation.[6] Cost-effective transition metals such as iron and copper, employing chlorine radicals produced *via* the photoinduced ligand-to-metal charge transfer (LMCT) process, have gained substantial attention as potent hydrogen atom transfer (HAT) agents in current research.[7] The development of these radical-mediated C–H functionalization reactions represents a substantial advancement in the formation of diverse chemical bonds.[8] However, a crucial point in the discussion of carbon–hydrogen activation revolves around the regioselectivity of hydrogen atom transfer. Apart from the diverse range and bulkiness of HAT species,[9] we propose that the use of radical acceptors plays a key role in influencing reaction selectivity.[8a,10] Taking 2,3-dimethylbutane as an example, the bond dissociation energy of 1° C(sp^3)–H bonds significantly exceeds that at 3° C(sp^3)–H bonds, implying a higher reactivity at the tertiary C(sp^3)–H bonds.[2b] Surprisingly, in Duan's and our investigations of photoinduced iron-catalyzed C(sp^3)–H borylation,[8a] thiolation,[8a,b] sulfinylation,[8a,b] phosphorylation[8c] and alkynylation reactions,[8i] the reaction sites predominantly showed 1° C–H selectivity, with no observation of C(sp^3)–H functionalization at the weak 3° C–H bonds (Scheme 1a).

To explore how other radical acceptors affect the regioselectivity of the C(sp^3)–H functionalization reactions, our attention turned towards iron photocatalytic C(sp^3)–H alkenylation. This shift arose from the potential of olefins in organic synthesis due to their remarkably diverse chemical reactivity encompassing addition and oxidation reactions. Thus, achieving direct alkenylation of simple alkanes holds significant synthetic potential in constructing and deriving complex molecules.[11] Iron and cobalt exhibit similar chemical properties and reactivity (Scheme 1b).[12] Due to the potential mutual interference in the redox processes of iron and cobalt catalysts within the reaction system, the exploration of their synergistic catalytic effects under photochemical conditions remains relatively limited in the current literature.[13] Electrocatalysis and photocatalysis have emerged as increasingly feasible platforms for sustainable molecular assembly by synergistically integrating electrochemical synthesis and photochemical oxidation–reduction catalysis within a single system. This approach eliminates the need for external chemical oxidants and reductants,

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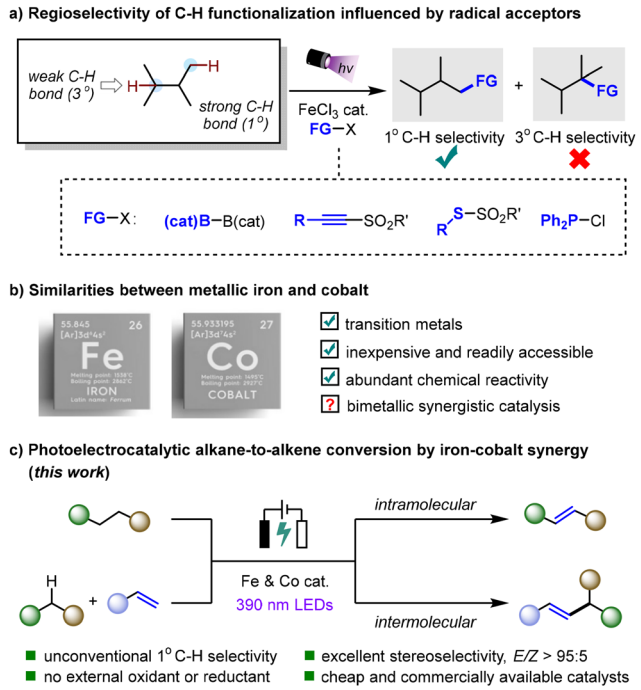


Scheme 1 C–H functionalization reactions *via* iron photocatalysis.

as the electric current serves as a clean electron source and sink to modulate the redox states of the catalysts.[14] Building on previous seminal work[8,14] and the superiority of the photoelectrocatalytic framework,[15] we envision exploring an innovative and sustainable platform for non-directed C(sp^3)–H functionalization employing iron–cobalt bimetallic catalysis. In our proposed strategy, the chlorine radicals formed under iron-induced light act as HAT species, while the generated Fe^{2+} undergoes oxidation at the anode.[8m] On the other hand, owing to its higher oxidation potential, Co^{3+} acts as a cathodic catalyst, enabling separate catalytic cycles for iron and cobalt at the anode and cathode, respectively, thereby preventing competitive reactions at the anode.[16]

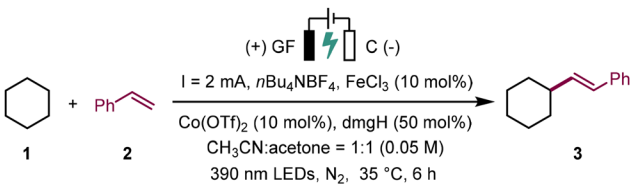
Herein, we report the successful realization of a photoelectrically synergistic induced iron/cobalt dual catalysis, enabling the non-directed C(sp^3)–H alkenylation reaction (Scheme 1c). Our C–H alkenylation protocol is applicable not only to simple alkanes and silanes but also to various ketones and nitriles. Furthermore, this photoelectric strategy appears to have a preference for stronger 1° C–H bonds, suggesting that alkenes, when used as radical acceptors, could potentially influence the selectivity of HAT.

Results and discussion

In the initial phase of our research, we selected cyclohexane **1** and styrene **2** as model substrates for condition optimization, with detailed experimental conditions outlined in Table 1. Graphite felt (GF) was employed as the anode, and graphite rod as the cathode, with the addition of $FeCl_3$, $Co(OTf)_2$, dimethylglyoxime (dmgH), and tetrabutylammonium tetrafluoroborate (nBu_4NBF_4) into the reaction system. Acetone : acetonitrile (v/v = 1 : 1) was used as solvent. Under nitrogen conditions, the reaction between **1** and **2** proceeded efficiently with a constant current of 2 mA, achieving an intermolecular C(sp^3)–H olefination reaction and yielding product **3** in 70% yield with exclusive *E*-selectivity (Table 1, entry 1). Subsequently, we tested several alternative electrolytes such as nBu_4NCl and nBu_4NPF_6, but unsatisfactory results were obtained (entries 2 and 3). Substituting the carbon felt anode with an aluminum rod or nickel sheet led to a significant decrease in the yield (entries 4 and 5). When copper chloride was used instead of iron chloride, the reaction scarcely proceeded (entry 6). The use of $Co(acac)_2$ and $CoSO_4$ as cobalt catalysts resulted in varying degrees of yield reduction (entries 7 and 8). Additionally, adjusting the operating current to 5 mA led to a slight decrease in the yield of alkylation products (entry 9). Furthermore, the reaction was subjected to solvent screening, revealing a drastic drop in yield to 40% when acetonitrile was used (entry 10), while trace of target product was detected with the use of acetone as solvent (entry 11). In the absence of dmgH, iron or cobalt catalyst, the reaction did not occur. Lack of electric current or light also prevented the reaction from proceeding, underscoring the crucial role of both electric current and light in this transformation (entries 12 and 13).

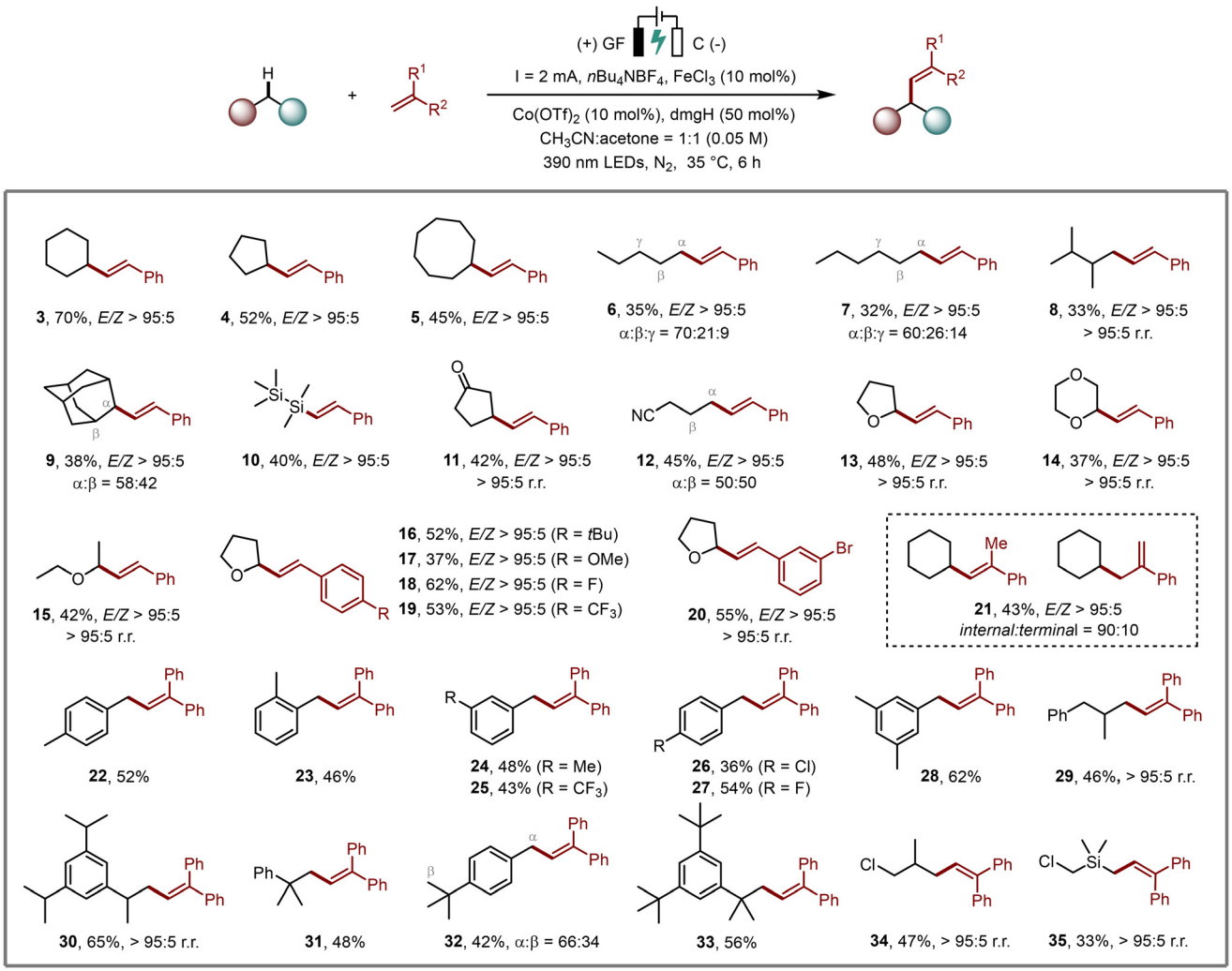
Upon establishing the optimal conditions, we initiated the substrate expansion for this photoinduced C(sp^3)–H olefina-

Table 1 Optimization studies[a]



Entry	Deviation from standard conditions	**3** [b] (%)
1	None	70
2	nBu_4NCl instead of nBu_4NBF_4	38
3	nBu_4NPF_6 instead of nBu_4NBF_4	35
4	Al plate as cathode	42
5	Ni plate as cathode	47
6	$CuCl_2$ instead of $FeCl_3$	<5
7	$Co(acac)_2$ instead of $Co(OTf)_2$	45
8	$CoSO_4$ instead of $Co(OTf)_2$	65
9	I = 5 mA	60
10	CH_3CN as solvent	40
11	Acetone as solvent	Trace
12	w/o dmgH, $FeCl_3$ or $Co(OTf)_2$	N.D.
13	w/o electricity or light	Trace

[a] Reaction conditions: **1** (2.0 mmol, 10.0 equiv.), **2** (0.20 mmol, 1.0 equiv.), $FeCl_3$ (10 mol%), $Co(OTf)_2$ (10 mol%), dmgH (50 mol%), nBu_4NBF_4 (2.0 equiv.), I = 2.0 mA, 6 h, CH_3CN : acetone = 1 : 1 (4.0 ml), 35 °C, 390 nm LEDs (18 W), graphite felt (GF) as anode, graphite rod as cathode, undivided cell. [b] Yields are of isolated products after chromatographic purification. dmgH: dimethylglyoxime. N.D.: not detected.



Scheme 2 Substrate scope of C(sp^3)–H alkenylation reaction. Reaction conditions: hydrocarbon substrate (2.0 mmol, 10.0 equiv.), alkene substrate (0.20 mmol, 1.0 equiv.), $FeCl_3$ (10 mol%), $Co(OTf)_2$ (10 mol%), dmgH (50 mol%), nBu_4NBF_4 (2.0 equiv.), *I* = 2.0 mA, 6 h, CH_3CN : acetone = 1 : 1 (4.0 ml), 35 °C, 390 nm LEDs (18 W), graphite felt (GF) as anode, graphite rod as cathode, undivided cell. Yields are of isolated products after chromatographic purification.

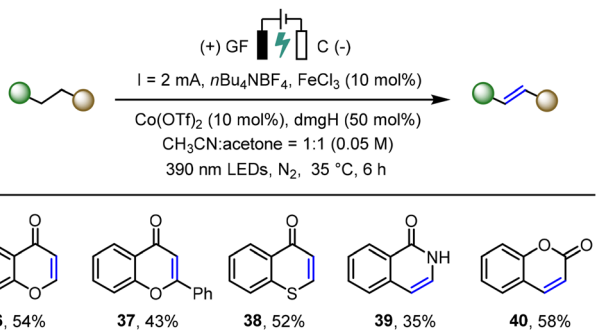
tion, systematically exploring a range of alkane and alkene derivatives (Scheme 2). Using styrene as the template substrate, we tested various alkanes. Gratifyingly, commonly used alkanes, silanes, ketones, nitriles, ethers, and others proved compatible with our photoredox system, delivering the desired products in acceptable yields with exclusive *E*-selectivity (**3–15**). For linear alkanes such as *n*-pentane, *n*-hexane, and 2,3-dimethylbutane, C(sp^3)–H alkenylation exhibited multiple reaction sites, yet the reaction predominantly occurred at the terminal methyl position. This terminal regioselectivity closely resembled previous reports, suggesting that alkenes as radical acceptors also influence reaction selectivity (**6–8**). In the case of adamantane, the reaction favored the less sterically hindered methylene positions (**9**). For the reaction of silanes, the reaction afforded the corresponding olefination products in reasonable yields (**10**). Furthermore, both cyclopentanone and butyronitrile underwent C(sp^3)–H olefination smoothly, demonstrating excellent functional group compatibility of the reaction (**11–12**). The observed regioselectivity is likely determined by the steric properties of both the HAT reagent and the radical acceptor. Next, we directed our attention towards the modification of ether compounds. The use of tetrahydrofuran, 1,4-dioxane, and ethyl ether all provided the desired products in moderate yields and excellent *E*/*Z* ratios (**13–15**). Additionally, using tetrahydrofuran as the model substrate, we expanded our investigation for the scope of alkenes. The results revealed that the reaction proceeded well regardless of whether styrenes bear electron-donating substituents on the aromatic rings such as *tert*-butyl and methoxy groups, or electron-withdrawing substituents such as halogens and trifluoromethyl groups (**16–20**). For α-methylstyrene as the alkenylic acceptor, the reaction with cyclohexane as the substrate presents two possible elimination pathways – olefin formation at the internal position and at the terminus. The reaction proceeded in 43% yield with a selectivity of 9 : 1 (internal : terminal) (**21**). Finally, we sought to test whether toluene

derivatives could serve as suitable alkyl substrates for the reaction. Unfortunately, when styrene was used as the olefin substrate, the reaction product had very similar polarity with the excess alkane substrate, making the isolation of pure products very challenging. Therefore, we opted to expand this part of the substrate scope by employing 1,1-diphenylethylene as the model substrate. The photoelectrochemical reaction of commonly used solvents such as *p*-xylene, *o*-xylene, and *m*-xylene afforded the corresponding alkene products in moderate yields (**22–24**). Toluene derivatives bearing trifluoromethyl groups or halogens on the aromatics underwent the photoelectrochemical reactions well to give products **25–27** in acceptable yields with exclusive *E*-selectivity. When 1,3,5-triisopropylbenzene participated in the reaction, regioselectivity of terminal methyl group was exclusively achieved (**30**). Similarly, *tert*-butylbenzene reacted to give product **31** as expected, while 4-methyl-*tert*-butylbenzene containing two reactive C(sp^3)–H sites predominantly underwent the reaction at the benzylic methyl group (**32**). 1,3,5-Tri-*tert*-butylbenzene also proceeded smoothly, yielding the corresponding alkene products (**33**). Furthermore, for chlorinated alkanes, the reaction worked well to afford the desired products in acceptable yields (**34–35**), which further demonstrated the generality of this reaction.

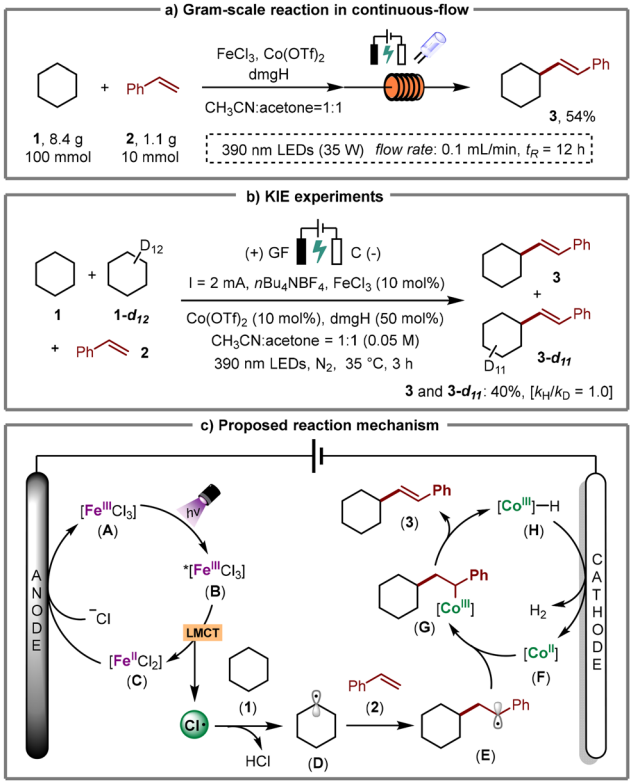
To delve into the capabilities of this photoelectrochemical strategy, we next successfully expanded its application to intramolecular dehydrogenation reactions *via* radical-mediated α-hydrogen (α-H) elimination process of various heteroatoms. As illustrated in Scheme 3, a series of dehydrogenation products could be achieved, encompassing compounds containing α-hydrogen of oxygen, sulfur, and nitrogen atoms (**36–40**).

To further showcase the synthetic potential of the iron/cobalt-photoinduced ligand-to-metal charge transfer (LMCT) method, we conducted a gram-scale continuous-flow reaction using cyclohexane (**1**) and styrene (**2**) as substrates, as depicted in Scheme 4a. By applying a flow rate of 0.1 mL min^{-1} and a reaction time of 12 hours, we were able to scale up the C(sp^3)–H alkenylation reaction by 50-fold. The reaction solution, upon purification, yielded the corresponding alkenylated product (**3**) in a 54% yield.

In order to gain deeper insights into the reaction mechanism, a series of mechanistic experiments were conducted (further details can be found in the ESI†). Kinetic isotope effect (KIE) experiments were conducted to probe whether



Scheme 3 Dehydrogenation reactions *via* iron & cobalt photocatalysis.



Scheme 4 Gram-scale reaction in continuous flow and mechanistic studies.

hydrogen atom transfer (HAT) serves as the rate-determining step in the overall reaction mechanism. The reaction of styrene with equimolar amounts of cyclohexane and deuterated cyclohexane under standard conditions of C–H alkenylation for 3 hours yielded a mixture of **3** and isotopically labeled **3-d_{11}** in 40% yield, with secondary kinetic isotope effects (k_H/k_D = 1.0), indicating that the hydrogen/deuterium atom abstraction step is not the turnover-limiting step in the iron/cobalt catalytic cycle (Scheme 4b).

Based on the aforementioned experimental results and literature survey,[8,17] a plausible mechanism for the iron/cobalt synergistic catalyzed C(sp^3)–H alkenylation reaction is proposed, as depicted in Scheme 4c. The process initiates with ligand-to-metal charge transfer from the excited state $FeCl_3$ catalyst (**B**), generating an electrophilic chlorine radical. This chlorine radical abstracts a hydrogen atom from cyclohexane (**1**), producing a reactive alkyl radical (**D**), while Fe(II) is oxidized to Fe(III) at the anode. Simultaneously, the formed alkyl radical undergoes addition to the alkene (**2**), generating an additional radical intermediate (**E**), which is subsequently captured by a Co(II) complex to form an organocobalt(III) complex (**G**). The crucial β-H elimination step readily occurs, yielding alkene compound (**3**) and a Co(III)–H intermediate (**H**). The reaction of the Co(III)–H complex with a proton leads to H_2 extrusion, followed by electrochemical reduction of the Co(III) complex at the cathode to regenerate the Co(II) complex, thus renewing the cobalt catalyst.

Conclusions

In summary, we describe an unprecedented photoelectrochemical synergistic strategy for the non-directed C(sp^3)–H alkenylation of inert alkanes using an iron–cobalt bimetallic catalytic system. Through the photo-induced ligand-to-metal charge transfer (LMCT) process and the electrochemical anodic oxidation coupled with cathodic reduction, combined with the synergistic catalysis of iron & cobalt, we have achieved research on the C(sp^3)–H alkenylation of unactivated alkanes. Experimental results indicate that alkenes, serving as radical acceptors, can also influence the regioselectivity of hydrogen atom transfer (HAT), with the observed preference for alkenylation at primary C–H bonds likely being determined by the steric properties of both the HAT reagent and the radical acceptor.

Data availability

Data for this article, including the ESI† are available at Organic Chemistry Frontiers at **https://doi.org/10.1039/D5QO00017C**. The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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