JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by MT ROYAL COLLEGE

Communication

Generation and Confinement of Long-lived N-oxyl Radical and its Photocatalysis

Chaofeng Zhang, Zhipeng Huang, Jianmin Lu, Nengchao Luo, and Feng Wang

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b12928 • Publication Date (Web): 24 Jan 2018

Downloaded from http://pubs.acs.org on January 24, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Generation and Confinement of Long-lived N-oxyl Radical and its Photocatalysis

Chaofeng Zhang,[a] Zhipeng Huang,[a,b] Jianmin Lu,[a] Nengchao Luo,[a,b] and Feng Wang[a*]

[a] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information Placeholder

ABSTRACT: Generation of controllable carbon radical under the assistance of N-oxyl radical is an efficient method for the activation of C–H bonds in hydrocarbons. We herein report that irradiation of α-Fe_2O_3 and N-hydroxyphthalimide (NHPI) under 455 nm light generates phthalimide-N-oxyl radical (PINO*), which after being formed by oxidation with holes, is confined on α-Fe_2O_3 surface. The half-life time of the confined radical reaches 22 seconds as measured by in situ electron paramagnetic resonance (EPR) after the light being turned off. This allows the long-lived N-oxyl radical to abstract the H from C–H bond to form a carbon radical that reacts with molecular oxygen to form $R_3C–OO•$ species, decomposition of which leads to oxygenated products.

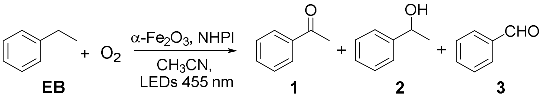
Selective oxidation of C(sp^3)–H bonds of hydrocarbons with molecular oxygen (O_2) is an essential tool in organic synthesis and industrial chemistry.[1] However, due to the spin-flip restriction between ground triplet state $^3\Sigma_g^-O_2$ and ground state substrate,[2] O_2 is generally unreactive under mild conditions,[3] and thus transition-metal catalysts are used to activate $^3\Sigma_g^-O_2$ to various active O* species.[4] Alternatively, the C–H bond can be first H-abstracted to form a carbon radical, which then reacts with molecular oxygen to produce oxygenated compounds.[5] A representative example is to employ N-oxyl radicals ($R_2NO•$) to abstract H of C–H bond.[6] But the generation of N-oxyl radicals from N-hydroxyl compounds (R_2NOH) requires radical initiators, such as azocompounds, peroxides, metal salts, NO_x, and quinones.[7] Therefore, exploring new methods for the generation of N-oxyl radical from N-hydroxyl compound is very important for C–H bond oxidation.[8]

Free N-oxyl radical is short-lived and over-reactive,[9] which brings out side reactions via the uncontrollable chain oxidation of hydrocarbon.[10] A long-lived but still active N-oxyl radical maybe beneficial for C–H bond activation.[11] A possible idea to extend the life time of N-oxyl radical is to avoid the recombination of $R_2NO•$ and the abstracted hydrogen of N-hydroxyl compounds. Based on this idea, confining and stabilizing the N-oxyl radical on solid support or catalyst that can also conveniently promote the generation of $R_2NO•$ from R_2NOH is proposed in the present study.

Metal oxides are frequently used catalysts in organic reactions.[12] When used as photocatalysts, pristine metal oxide surface is usually lack of photocatalytic center to adsorb and cleave the C–H bond of hydrocarbons into a carbon radical. Besides, the wide band gap and/or fast recombination of photogenerated hole (h^+) and electron (e^-) remains obstacles for photo harvesting. Solving these issues by introducing defect level[13] and substrate modification[12a, 12b] have been studied. In addition, adding free photosensitizer to introduce e^- or adding h^+ acceptor to transfer surface h^+ can restrain their recombination.[12b, 12d, 14]

The h^+ of some metal oxides is able to oxidize ROH/RNH_2 to RO^+H/RN^+H_2.[12a, 12c] Then we hypothesize that the h^+ of oxides with appropriate valence band potential can also oxidize R_2NOH to $R_2NO•$, which can promote the H-abstraction of C–H bond to a carbon radical. Further exploration found α-Fe_2O_3 was the desired semiconductor. A representative R_2NOH structure, NHPI, can adsorb on α-Fe_2O_3 surface and promote the separation of h^+ and e^- by reaction with h^+. The generated N-oxyl radical is confined on α-Fe_2O_3 surface and has an unexpected long life time.

Table 1. Photocatalytic oxidation of ethylbenzene [a]



Entry	Catalyst	Additive (0.1 mmol)	Conv. (%)	GC selectivities (%)		
				1	2	3
1	α-Fe_2O_3	-	0	-	-	-
2	α-Fe_2O_3 + NHPI	-	74	99	0	1
3[b]	α-Fe_2O_3 + NHPI	-	0	-	-	-
4	NHPI	-	0	-	-	-
5[c]	α-Fe_2O_3 + NHPI	-	55	96	2	2
6[c]	α-Fe_2O_3 + NHPI	BHT	0	-	-	-
7[c]	α-Fe_2O_3 + NHPI	Na_2S	0	-	-	-
8[c]	α-Fe_2O_3 + NHPI	$(NH_4)_2C_2O_4$	0	-	-	-
9[c]	α-Fe_2O_3 + NHPI	$AgNO_3$	43	99	0	trace
10[c]	α-Fe_2O_3 + NHPI	BQ	47	81	17	2

[a] Reaction conditions: α-Fe_2O_3 10 mg, ethylbenzene 0.1 mmol, NHPI 3 mg, CH_3CN 1.0 mL, O_2 1 atm, blue LED light (455 nm, 18 W), 40 °C, 10 h; symbol - means no additive or no product; [b] no light; [c] 4 h.

Although α-Fe_2O_3 has a band gap of 2.20 eV, with a 0.28 eV conduction band (CB) and 2.48 eV valence band (VB), which could be a photocatalyst under visible light, α-Fe_2O_3 alone could not catalyze the ethylbenzene oxidation under 455 nm irradiation (Table 1, entry 1). A combination of α-Fe_2O_3 and NHPI can promote the reaction with a 73% acetophenone yield (entry 2). Control experiments confirm the reaction is a photocatalytic process (entry 3), and both NHPI and α-Fe_2O_3 are necessary (entries 1, 2 and 4).

The inhibition effect of 2,6-di-tert-butyl-4-methylphenol (BHT), as a radical scavenger, indicates that this reaction contains a carbon radical intermediate (entry 6). The detection of butane-2,3-diyldibenzene under Ar condition suggests that the radical may be 1-phenethyl carbon radical (Figure S1). The necessity of h^+ of α-Fe_2O_3 in the reaction was confirmed by adding sodium sulfide or ammonium oxalate as hole capture reagent (entries 7-8).[15] Adding $AgNO_3$ as the e^- capture reagent and 1,4-benzoquinone (BQ) as the capture reagent for $O_2^{\bullet-}$ species could not inhibit the reaction (entries 9 and 10),[15a] in comparison with the reaction without additive (entry 5). These experiments conclude that the oxidation reaction requires the photo-generated h^+ rather than e^-.

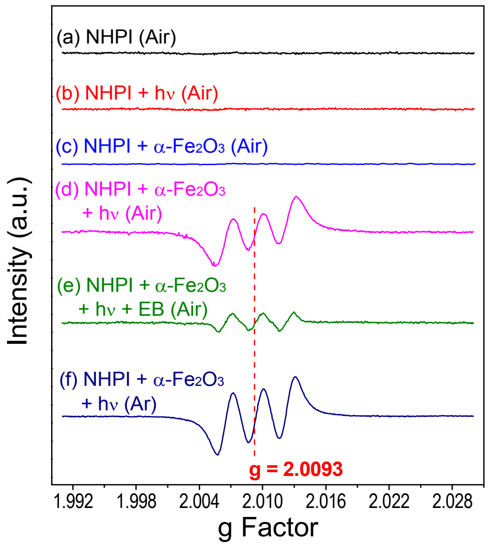


Figure 1. EPR measurements. Conditions: solvent CH_3CN, 455 nm blue LED light, and ambient air unless noted. Details can be found in the SI. (a) NHPI; (b) (a) + 10 min light; (c) NHPI + α-Fe_2O_3; (d) (c) + 10 min light; (e) (c) + ethylbenzene + 10 min light; (f) (c) under Ar atmosphere and 10 min light.

Although, the 455 nm irradiation (about 2.7 eV) may induce the separation of h^+ and e^- in α-Fe_2O_3 (band gap 2.20 eV), the h^+ of the α-Fe_2O_3 alone could not cleave the C_α–H bond of ethylbenzene to a carbon radical. However, adding NHPI can trigger the oxidation. The controlled experiment without O_2 offered a product of 2-(1-phenylethoxy)isoindoline-1,3-dione (Figure S1), which indicated the role of PINO radical in the H-abstraction at the benzylic site.[16] Above experimental results also suggest a relationship between photo-generated h^+ and PINO generation.

In-situ EPR was used to explore the generation of PINO radical under visible irradiation. Tests with and without 455 nm irradiation could not generate PINO from NHPI (Figure 1a and 1b). An obvious triplet EPR signal appeared in the combination of α-Fe_2O_3 and NHPI under 455 nm irradiation (Figure 1c and 1d). The g factor of this triplet signal is 2.0093, indicating the PINO* radical is formed (g=2.0073).[7a] When ethylbenzene was added in the above solution (Figure 1e), the signal of PINO* radical decreased by 60%, inferring the reaction between PINO* radical and ethylbenzene. When the EPR test of NHPI and α-Fe_2O_3 was carried out in Ar (Figure 1f), PINO* radical was still generated, showing that the formation of PINO* did not need oxygen. This phenomenon concludes the key role of h^+ on the generation of N-oxyl radical.

According to Pedulli's report,[17] the electron-withdrawing carbonyl groups reduce the mesomeric structures of N-oxyl radical with charge separation (Scheme S1), which makes PINO less stable and increases the R2NO–H bond dissociation enthalpy (BDE) of NHPI. Besides, NHPI tends to generate an intramolecular hydrogen bond, which is absent in the PINO radical. Given the fact that the BDE of R2NO–H bond of NHPI in CH_3CN is about 368.4 kJ·mol^{-1} (3.82 eV),[17] it is hard for the direct homolysis of R_2NO–H bond under 455 nm irradiation (about 2.7 eV). Instead, NHPI may first adsorb and get activated on α-Fe_2O_3 surface, followed by being oxidized by holes to the confined PINO* radical. This postulation is experimentally confirmed by the photocatalytic oxidation of a sterically-hindered substrate, triphenylmethane (Ph_3C-H). Only 3% conversion was obtained under the identical conditions (Scheme S2A). In comparison, the combined homogeneous catalyst of $NaNO_2$/DDQ/NHPI, which generates unconstrained PINO radical,[7b, 7c] gave 98% conversion at 100 °C in 3 h (Table S1, entry 1). We attribute the difference to that the formed PINO* is confined on α-Fe_2O_3 surface. As such, the close contact between the N-oxyl radical and C(sp^3)–H bond of triphenylmethane is impeded (Figure S2). This confinement effect may partly explain the g-factor of the generated PINO* is slightly less than that of the free PINO.

The state of adsorbed NHPI* on α-Fe_2O_3 surface was confirmed by FTIR (Figure 2). The apparent red shift of C=O vibration at 1711 cm^{-1} of free NHPI to 1681 cm^{-1} of the adsorbed NHPI* indicates the interaction between carbonyl groups and α-Fe_2O_3 surface. The red-shift of aromatic ring skeleton vibration (1483 cm^{-1} to 1467 cm^{-1}; 1466 cm^{-1} to 1446 cm^{-1}) and the appearance of peaks between 1526 and 1585 cm^{-1} signifies the adsorption of aromatic ring on α-Fe_2O_3 surface. FTIR results suggest NHPI molecules lie down on α-Fe_2O_3 surface, facilitating electron transfer. It should be noted that the direction of electron transfer from catalyst to these functional groups is different from the one from NHPI* to α-Fe_2O_3 h^+ during R_2NO–H oxidation under light.

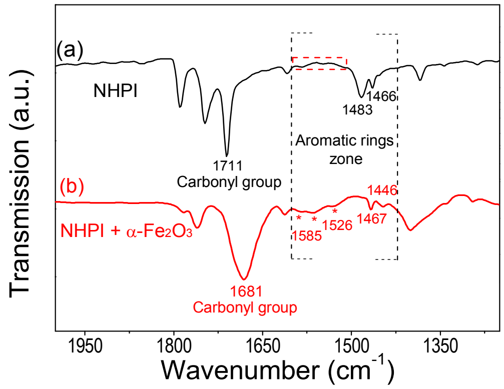


Figure 2. FTIR spectra of (a) NHPI and (b) adsorbed NHPI* on α-Fe_2O_3.

In situ EPR tests were conducted to study the behavior of confined PINO* (Figure S3). When the mixture of NHPI and α-Fe_2O_3 was irradiated with 455 nm light, the PINO radical triplet signal immediately appeared and remained as along as the light was on. When the light was turned off, the EPR signal decayed to zero in more than 200 seconds. The half-life time of PINO* was measured to be 22 seconds (Figure 3 and Table S2, see the calculation of half-time), which was quite different from the free but shorted-lived PINO.[9, 18] Baciocchi in his works mentioned that the PINO signal of time-resolved spectrum is stable on the millisecond time scale.[18] Although the confinement effect makes PINO* a long-lived N-oxyl radical, given the EPR characterization obtained above (Figure 1d and 1e), the PINO* is still active in abstracting H from hydrocarbon substrate.

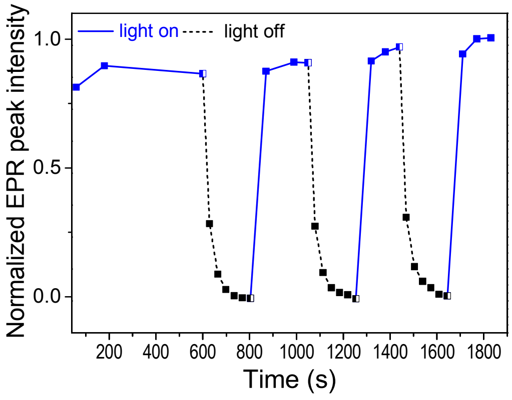


Figure 3. In situ EPR light on-off tests. Experimental conditions: 10 mg NHPI and 10 mg α-Fe_2O_3 are dispersed in 1.0 mL acetonitrile under Ar. The value of EPR signal (Figure S3) nearby G=3314.62 marks the relative change of PINO*. All signals are normalized to the highest signal intensity.

Based on above results, the photo-oxidation of ethylbenzene to acetophenone may proceed as the following (Figure 4). (i) The 455 nm light irradiation generates h^+ and e^- in α-Fe_2O_3. (ii) The h^+ of α-Fe_2O_3 oxidizes the absorbed NHPI* to PINO* and H^+ species. (iii) The H^+ shifts to CB band, where reacts with O_2 and get reduced by e^- to form H_2O via a possible H_2O_2 intermediate,[19] and the detailed discussion can be found in the SI. (vi) The confined PINO* then abstracts an H from C–H bond and restores to the adsorbed NHPI* for the next catalytic cycle. (v) It is known process that $PhCH{\bullet}CH_3$ radical reacts with O_2 to form $PhCH(OO{\bullet})CH_3$ and then transforms to $PhCH(OOH)CH_3$, whose selective decomposition leads to $PhCOCH_3$.[6b]

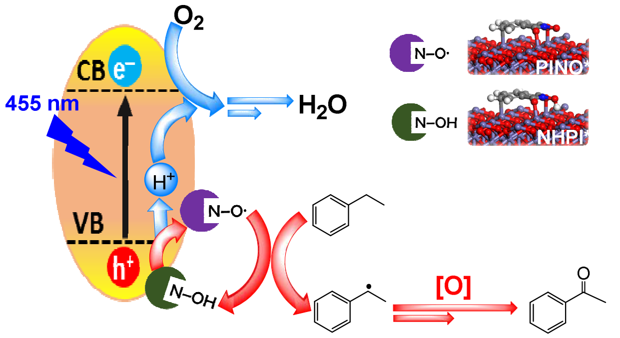
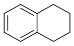
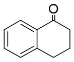
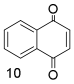
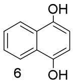
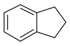
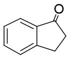
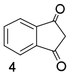
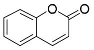
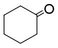
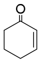
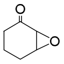
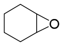
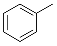
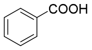
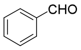
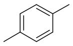
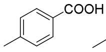
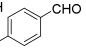


Figure 4. Proposed mechanism of ethylbenzene photoxidation over α-Fe_2O_3 and NHPI.

We also explored the feasibility of this catalytic system in the photo-oxidation of other substrates at $C(sp^3)$–H bond position (Table 2). The substrates with an R–CH_2–R structure tended to give ketone products (entries 1-4). The reaction occurs at C_α site for Ar–$C_\alpha H_2$–R. Side methyl or methylated benzene Ar-CH_3 gave acids as the main products (entries 5 and 6).

Table 2. Photoxidation of $C(sp^3)$–H bonds with NHPI and α-Fe_2O_3[a]

Entry	Substrate	Time (h)	Conversion (%)	Products distribution (%)
1		1.5	97	 83  10  6
2		1.0	99	 91  4  4
3		12	9	 99
4		0.5	98	 83  9  6
5		12	52	 86  13
6		12	93	 96  4

[a] Reaction condition: substrate 0.05 mmol, NHPI 3.0 mg, α-Fe_2O_3 10 mg, acetonitrile 1.0 mL, O_2 1 atm, 40 °C, blue LED light (455 nm, 18 W).

In conclusion, we here report a novel strategy of the generation and confinement of N-oxyl radical on α-Fe_2O_3 surface. Combined characterizations and measurements suggest the adsorbed NHPI* can promote the separation of hole and electron on α-Fe_2O_3 surface by consuming the hole of α-Fe_2O_3 by virtue of the transformation of NHPI* to a confined PINO* radical. This confined and long-lived PINO* radical is required for efficient oxidation of hydrocarbons with molecular oxygen to oxygenated compounds. This study offers a new way of utilizing organic radical in selective oxidation.

ASSOCIATED CONTENT

Supporting Information.

Experiment process, controlled experiments and discussions. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

wangfeng@dicp.ac.cn

Notes

The authors declare no competing financial interest.

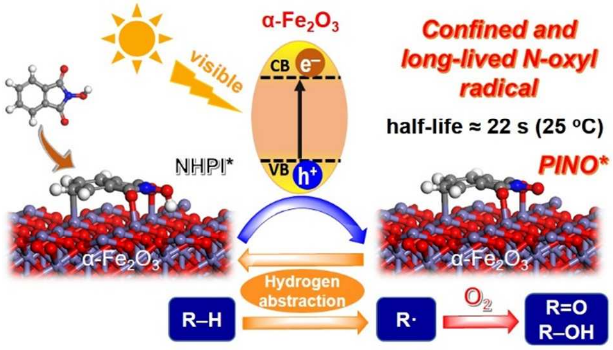
ACKNOWLEDGMENT

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No.XDB17020000), National Natural Science Foundation of China (21690082, 21690084 and 21690080).

REFERENCES

1. (a) Fokin, A. A.; Schreiner, P. R. *Chem. Rev.* **2002,** *102*, 1551-1593; (b) Stahl, S. S. *Science* **2005,** *309*, 1824-1826.
2. Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003,** *103*, 1685-1757.
3. Borden, W. T.; Hoffmann, R.; Stuyver, T.; Chen, B. *J. Am. Chem. Soc.* **2017,** *139*, 9010-9018.
4. (a) Nosaka, Y.; Nosaka, A. Y. *Chem. Rev.* **2017,** *117*, 11302-11336; (b) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005,** *105*, 2329-2363.
5. Mayo, F. R. *Acc. Chem. Res.* **1968,** *1*, 193-201.
6. (a) Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001,** *343*, 393-427; (b) Yang, G. Y.; Ma, Y. F.; Xu, J. *J. Am. Chem. Soc.* **2004,** *126*, 10542-10543; (c) Lauber, M. B.; Stahl, S. S. *ACS Catal.* **2013,** *3*, 2612-2616; (d) Yan, Y. P.; Feng, P.; Zheng, Q. Z.; Liang, Y. F.; Lu, J. F.; Cui, Y. X.; Jiao, N. *Angew. Chem. Int. Ed.* **2013,** *52*, 5827-5831; (e) Ghosh, S.; Castillo-Lora, J.; Soudackov, A. V.; Mayer, J. M.; Hammes-Schiffer, S. *Nano Lett.* **2017,** *17*, 5762-5767; (f) Rahimi, A.; Azarpira, A.; Kim, H.; Ralph, J.; Stahl, S. S. *J. Am. Chem. Soc.* **2013,** *135*, 6415-6418; (g) Hoover, J. M.; Ryland, B. L.; Stahl, S. S. *J. Am. Chem. Soc.* **2013,** *135*, 2357-2367.
7. (a) Recupero, F.; Punta, C. *Chem. Rev.* **2007,** *107*, 3800-3842; (b) Zhou, L. P.; Zhang, C. F.; Fang, T.; Zhang, B. B.; Wang, Y.; Yang, X. M.; Zhang, W.; Xu, J. *Chin. J. Catal.* **2011,** *32*, 118-122; (c) Zhang, C. F.; Li, H. J.; Lu, J. M.; Zhang, X. C.; MacArthur, K. E.; Heggen, M.; Wang, F. *ACS Catal.* **2017,** *7*, 3419-3429.
8. (a) Zhang, P.; Wang, Y.; Yao, J.; Wang, C.; Yan, C.; Antonietti, M.; Li, H. *Adv. Synth. Catal.* **2011,** *353*, 1447-1451; (b) Rafiee, M.; Miles, K. C.; Stahl, S. S. *J. Am. Chem. Soc.* **2015,** *137*, 14751-14757; (c) Luo, J.; Zhang, J. *J. Org. Chem.* **2016,** *81*, 9131-9137; (d) Badalyan, A.; Stahl, S. S. *Nature* **2016,** *535*, 406-410.
9. (a) Baciocchi, E.; Bietti, M.; Di Fusco, M.; Lanzalunga, O.; Raponi, D. *J. Org. Chem.* **2009,** *74*, 5576-5583; (b) Mazzonna, M.; Bietti, M.; DiLabio, G. A.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2014,** *79*, 5209-5218; (c) Capraro, M. G.; Franchi, P.; Lanzalunga, O.; Lapi, A.; Lucarini, M. *J. Org. Chem.* **2014,** *79*, 6435-6443.
10. Zhou, L. P.; Chen, Y.; Yang, X. M.; Su, Y. L.; Zhang, W.; Xu, J. *Catal. Lett.* **2008,** *125*, 154-159.
11. Ryland, B. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *J. Am. Chem. Soc.* **2014,** *136*, 12166-12173.
12. (a) Furukawa, S.; Ohno, Y.; Shishido, T.; Teramura, K.; Tanaka, T. *ACS Catal.* **2011,** *1*, 1150-1153; (b) Leow, W. R.; Ng, W. K. H.; Peng, T.; Liu, X. F.; Li, B.; Shi, W. X.; Lum, Y.; Wang, X. T.; Lang, X. J.; Li, S. Z.; Mathews, N.; Ager, J. W.; Sum, T. C.; Hirao, H.; Chen, X. D. *J. Am. Chem. Soc.* **2017,** *139*, 269-276; (c) Zavahir, S.; Xiao, Q.; Sarina, S.; Zhao, J.; Bottle, S.; Wellard, M.; Jia, J. F.; Jing, L. Q.; Huang, Y. M.; Blinco, J. P.; Wu, H. S.; Zhu, H. Y. *ACS Catal.* **2016,** *6*, 3580-3588; (d) Zhang, M. A.; Chen, C. C.; Ma, W. H.; Zhao, J. C. *Angew. Chem. Int. Ed.* **2008,** *47*, 9730-9733; (e) Hou, T. T.; Luo, N. C.; Li, H. J.; Heggen, M.; Lu, J. M.; Wang, Y. H.; Wang, F. *ACS Catal.* **2017,** *7*, 3850-3859; (f) Chen, H. J.; Liu, C.; Wang, M.; Zhang, C. F.; Luo, N. C.; Wang, Y. H.; Abroshan, H.; Li, G.; Wang, F. *ACS Catal.* **2017,** *7*, 3632-3638.
13. Di Valentin, C.; Pacchioni, G. *Acc. Chem. Res.* **2014,** *47*, 3233-3241.
14. Olshansky, J. H.; Ding, T. X.; Lee, Y. V.; Leone, S. R.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2015,** *137*, 15567-75.
15. (a) Li, Y.; Ouyang, S.; Xu, H.; Wang, X.; Bi, Y.; Zhang, Y.; Ye, J. *J. Am. Chem. Soc.* **2016,** *138*, 13289-13297; (b) Luo, N. C.; Wang, M.; Li, H. J.; Zhang, J.; Liu, H. F.; Wang, F. *ACS Catal.* **2016**, 7716-7721.
16. Wentzel, B. B.; Donners, M. P. J.; Alsters, P. L.; Feiters, M. C.; Nolte, R. J. M. *Tetrahcdron* **2000,** *56*, 7797-7803.
17. Amorati, R.; Lucarini, M.; Mugnaini, V.; Pedulli, G. F.; Minisci, F.; Recupero, F.; Fontana, F.; Astolfi, P.; Greci, L. *J. Org. Chem.* **2003,** *68*, 1747-1754.
18. (a) Baciocchi, E.; Bietti, M.; Di Fusco, M.; Lanzalunga, O. *J. Org. Chem.* **2007,** *72*, 8748-8754; (b) Baciocchi, E.; Bietti, M.; D'Alfonso, C.; Lanzalunga, O.; Lapi, A.; Salamone, M. *Org. Biomol. Chem.* **2011,** *9*, 4085-4090.
19. (a) Zhang, N.; Li, X. Y.; Ye, H. C.; Chen, S. M.; Ju, H. X.; Liu, D. B.; Lin, Y.; Ye, W.; Wang, C. M.; Xu, Q.; Zhu, J. F.; Song, L.; Jiang, J.; Xiong, Y. J. *J. Am. Chem. Soc.* **2016,** *138*, 8928-8935; (b) Li, X.; Yu, J.; Jaroniec, M. *Chem. Soc. Rev.* **2016,** *45*, 2603-2636; (c) Bi, D. Q.; Xu, Y. M. *J. Mol. Catal. A: Chem.* **2013,** *367*, 103-107.

TOC Graphic


α-Fe$_2$O$_3$
visible
CB
e⁻
VB
h⁺
NHPI*
Confined and long-lived N-oxyl radical
half-life ≈ 22 s (25 °C)
PINO*
α-Fe$_2$O$_3$
α-Fe$_2$O$_3$
Hydrogen abstraction
R–H
R·
O$_2$
R=O
R–OH