

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Shi, H. Hao, X. Li and X. Lang, *Catal. Sci. Technol.*, 2018, DOI: 10.1039/C8CY01096J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/catalysis

MergingtheCatechol-TiO2ComplexPhotocatalysis with TEMPO for Selective AerobicOxidation of Amines into Imines[†]

Ji-Long Shi,^a Huimin Hao,^a Xia Li, ^a and Xianjun Lang^{*a}

^a College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
*To whom correspondence should be addressed (X. J. Lang). E-mail: <u>xianjunlang@whu.edu.cn</u>
[†] TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl

Keywords: catechol • surface complex • titanium dioxide • visible light photocatalysis • oxidation of amines

Abstract: Catechol and its derivatives are model compounds to investigate the binding dynamics and photo-induced interfacial charge transfer events between an organic molecule and TiO₂. However, the practical potential of this process has received little attention in part due to the conceived instability of these molecules on TiO₂ under light irradiation. Herein, we present a new paradigm for selective oxidation of amines into imines with atmosphere O₂ by exploring the surface complexation of catechol derivatives on TiO₂ that give rise to visible-light-induced events of charge transfer. Our success depends on the merger of visible light photocatalysis of catechol surface complexed TiO₂ with TEMPO catalysis. With 5 mol% of TEMPO as a co-catalyst and catechol-TiO₂ complex (containing 0.8 mol% of catechol) as a photocatalyst, amines can be

View Article Online DOI: 10.1039/C8CY01096J

efficiently oxidized into imines with atmosphere O₂ under irradiation of blue light emitting diodes. Our work suggests that a suitable co-catalyst is the key to significantly expand the dimension of visible light photocatalysis for selective chemical transformations.

1. Introduction

Photo-induced charge transfer occurring at the interface between an organic molecule and TiO₂ underpins a variety of energy and environmental applications and therefore receives much attention.¹⁻³ The experimental and theoretical challenges during the investigation on these intricate and complicated reaction networks necessitates model compounds to simplify the overall process, consequently giving a unambiguous picture on the reaction details. Because of their simple molecular structures, catechol and its derivatives turn out to be excellent model molecules to study the interfacial charge transfer and binding dynamics occurrence on the surface of TiO₂. Especially, much effort has been directed towards the understanding the binding and charge transfer dynamics of these organic molecules on TiO₂, armed with a series of spectroscopic^{4, 5}, computational tools^{6, 7} or combined tools⁸. In most of these cases, catechol and its derivatives function as a convenient choice to mimic the behavior of complex dye molecules on TiO₂ which is only of fundamental value. To achieve the application of catechol-TiO₂ complex under realistic experimental conditions is a quite challenging undertaking.

However, decades of intensive effort to interpret the fundamental aspect of catechol-TiO₂ complex did pay off to guide the development of system to apply it into real photocatalytic operation. Several works emerged to prove the ability of catechol-TiO₂ in implementing visible light photocatalytic generation of H₂ from sacrificial agents.⁹⁻¹¹ In addition, the photocatalytic reduction of Cr(VI) to Cr(III) was also disclosed.¹¹ One recent work even suggests the possibility

View Article Online DOI: 10.1039/C8CY01096J

for photoelectrochemically oxidation of H₂O to O₂ with the same complex via an oxidation of catechol to semiquinone step.¹² Quinones, abundant in nature, are the core components for bioinspired oxidation catalysis.^{13, 14} Thus, we want to develop a paradigm for visible-light-induced selective aerobic oxidation with the *ortho*-quinone catalysis from oxidatively quenching of photoexcited catechol-TiO₂ complex. However, one primary concern is the stability of surface complexed catechols to sustain the photocatalytic process, since they are quite fragile molecules that usually need to be protected from oxidative damages and light irradiation for the purpose of storage.

For the generation of H₂ from sacrificial agents or the reduction of Cr(VI), the reducing agents are in excess which leads the overall reaction environment to be a reductive one that can make sure the tenacity of catechol-TiO₂ complex photocatalyst to a large extent. On the contrary, for the selective aerobic oxidation, O₂ is supplied in excess to achieve the target results which in turn engenders a predominantly oxidative circumstance. In effect, the photodegradation of catechol on TiO₂ surface under oxidative conditions was well-established by several previous reports.^{15, 16} Therefore, the maintenance of intactness of catechol-TiO₂ complex is an issue of major consideration that needs to be resolved. Moreover, the selective aerobic oxidation amines into imines was a very popular reaction in demonstrating the activity of ZnIn₂S₄¹⁷ or NH2-MIL-125(Ti) metal organic framework¹⁸. Particularly, visible light activity of NH2-MIL-125(Ti) was attributed to the ligand-to-metal charge transfer between 2-aminoterephthalate and Ti which was quite similar to the catechol-TiO₂ complex. Since quinone catalysis have a proven track record for the aerobic oxidation of amines,¹⁹ we selected this particular reaction to demonstrate our effort in transforming catechol-TiO₂ complex into a functional photocatalyst for selective aerobic oxidation. Our success depends on the merger of visible light photocatalysis with TEMPO catalysis to devise

selective chemical transformations,²⁰ a special case of the concept of cooperative photocatalysis advanced recently by us^{21} and others²².

2. Experimental

2.1 Light source

The light-emitting diodes (LEDs) were supplied by Shenzhen Qilai Optoelectronics Science and Technology Co., LTD., China. The reaction was usually irradiated with blue LEDs. In detail, four LED lamps were fastened around a magnetic stirrer in a circle in which the light irradiation was centered on the 10 mL Pyrex vessel. For blue LEDs, the irradiating wavelength range is 460 \pm 10 nm. Thus, the possible heating of the reaction medium by infrared light and possible leaking of UV light are completely excluded.

2.2 UV-Visible spectra

The UV-visible absorption spectra of the solid samples were recorded on a Shimadzu UV-2700 UV-VIS spectrophotometer with a diffuse reflectance measurement accessary. The UVvisible absorption spectra of the solutions were also carried out with the same equipments with a normal operating mode.

2.3 PXRD

Published on 03 July 2018. Downloaded by University of Michigan, Flint on 7/3/2018 10:11:27 AM.

The phase composition of the anatase TiO₂ sample was identified by powder X-ray diffraction (PXRD) using a Bruker D8 Advances diffractometer.

2.4 BET

The specific surface areas were determined by N₂ physisorption by using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum $(<1\times10^{-5}bar)$ in the Micromertics system at 120°C for 12 h prior to N₂ physisorption.

2.5 ESR

The ESR experiments were carried out on an electron spin resonance (ESR) spectrometer (JEOL, JES-FA200). The catechol-TiO₂ complex photocatalyst under the standard conditions was irradiated in the light chamber of the ESR spectrometer irradiated by a high-pressure Hg lamp with a filter to select the band of 460 nm visible light.

2.6 GC and GC-MS

The gas chromatography (GC) quantitative measurements of conversions of substrates and selectivities of products were made on a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) using high pure N₂ as the carrier gas and an Agilent J & W DB-5 capillary column (30 m \times 0.32 mm \times 0.25 µm, 19091J-413).

GC-FID standard analysis conditions: injector temperature 250 °C, detector temperature 280 °C, column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 20 °C/min. The results were all obtained using a split mode with a split ratio is 30:1.

Gas chromatography–mass spectrometry (GC–MS) analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a Shimadzu GCMS-QP2010 Ultra electron ionization mass spectrometer using a Restek (Rxi \mathbb{R} -5Sil MS) capillary column (30 m × 0.25 mm × 0.25 μ m) with high pure He as the carrier gas.

2.7 General procedure for the selective oxidation of amine into imine with air

In a typical reaction, 50 mg TiO₂, 2.4×10^{-3} mmol of **CAT D**, 0.3 mmol of primary benzylamine and 0.015 mmol of TEMPO were added to 1 mL of CH₃CN in a 10 mL pyrex vessel. For the oxidation of secondary amines, 0.2 mmol of secondary amines, 50 mg TiO₂, 2.4×10^{-3} mmol of benzenediol, and 0.015 mmol of TEMPO were added to the reaction vessel. For 5 min of

View Article Online DOI: 10.1039/C8CY01096J

ultrasonication, then the reaction mixture was stirred for 1h in dark to reach adsorption equilibrium. The 10 mL reaction Pyrex vessel was capped with butyl rubber septum. Then a rubber hole puncher was used to punch a hole in the rubber septum to connect with air to supply the oxygen demand in the experimental process. The reaction mixture was magnetically stirred at 1500 rpm and illuminated with blue LEDs in an air-conditioned room with additional electronic fan cooling to warrant the reaction temperature constantly at room temperature. At the end of reaction, the catechol-TiO₂ particles were separated from the reaction mixture by centrifugation and the products were quantitatively analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) using chlorobenzene as the internal standard. The structures of products were confirmed by comparison with the retention time with authentic samples and further confirmed by gas chromatography–mass spectrometry (GC-MS).

3. Results and discussion

Table 1. Different benzenediols complexed with TiO₂ merged with TEMPO on the visible-lightinduced selective oxidation of benzylamine with air ^[a]

	2 NH ₂ Benzenediol-TiO ₂ complex 5 mol% TEMPO, 1 atm air 3 W blue LEDs, CH ₃ CN		(1)
Entry	Benzenediol	Conv.[%] ^[b]	Sel.[%] ^[b]
1	1,2-Benzenediol	55	90
2	1,3-Benzenediol	26	89
3	1,4-Benzenediol	16	86

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of benzenediol, 50 mg of TiO₂, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH₃CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

The binding of catechol onto TiO₂ occurs very quickly without the assistance of extra conditions. We developed a technique by introducing precise amount of solution of catechol into the TiO₂ suspension to afford catechol-TiO₂ complex to conduct the selective oxidation of benzylamine with O₂ directly in the presence of TEMPO. In this fashion, thorough investigation to correlate different benzenediols with photocatalytic activity under visible light irradiation. All three benzenediols including 1,2-benzenediol (CAT A), 1,3-benzenediol and 1,4-benzenediol were screened to assess their influence on the selective oxidation of amines with O_2 in air (eq. 1). We were very pleased to find that three benzenediols can enhance the selective oxidation in all cases (entries 1-3, Table 1), but catechol gave the best results (entry 1, Table 1). CAT A binds with the Brønsted acid sites of TiO₂ through bidentate mononuclear linkage; whilst the linkage for the other benzenediols is bidentate binuclear one. Surface complex interaction between benzenediols and anatase TiO₂ decreased from CAT A to 1,3-benzenediol and 1,4-benzenediol.²³ This is the same order of conversions of benzylamines, ascribing to visible light absorption of benzenediol-TiO₂ complex. There was previous a large π system, graphene, complexed with TiO₂ as a photocatalyst for the selective aerobic oxidation of amines.²⁴ It is guite remarkable to find out that a small molecule like CAT A can be so efficient in implementing selective aerobic oxidation on TiO₂ under visible light irradiation.

View Article Online DOI: 10.1039/C8CY01096J

Table 2. Different substituted catechol complexed with TiO2 merged with TEMPO on the

visible-light-induced selective oxidation of benzylamine with air [a]

	HO HO CAT A	HO HO CAT B	HO HO CAT C	HO HO CAT D	
		соон но.	CHO CAT F	HO t-Bu HO CAT G	
Entry	Catechols		Conv.[%] ^[b]	Sel.[%] ^[b]
1	CAT A		55		90
2	CAT B		48		94
3	CAT C		57		98
4	CAT D		68		98
5	CAT E		49		93
6	CAT F		61		94
7	CAT G		36		84

[a] Reaction conditions: 0.3 mmol of benzylamine, 2.4×10^{-3} mmol of catechols, 50 mg of TiO₂, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH₃CN, 45 min. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Encouraged by the knowledge that CAT A delivers the best result for visible-light-induced aerobic oxidation of benzylamine, we studied the influence of substituted groups of catechols on the photocatalytic selective aerobic oxidation of benzylamines (Table 2). There are two positions in the phenyl ring of catechol that can be occupied by substituted group, i.e. the position 3 and the position 4. First, we used an electron donating group of -OCH₃ and electron withdrawing group of -CN to be in the position 3 of catechols, CAT B and CAT C, -OCH₃ giving slight worse result (entry 2, Table 2) and -CN giving almost the same results (Entry 3, Table 2) in comparison with that of catechol (entry 1, Table 2). However, if the -CN group were anchored in the position 4 of catechol, CAT D, evident increase in the conversion of benzylamine was observed (entry 4, Table 2). Nevertheless, another two electron withdrawing groups like -COOH and -CHO at the position 4 of catechol, CAT E and CAT F gave varied results (entries 5 and 6, Table 2), one is negative and the other is positive. This might be attributed to the high tendency of -COOH to adsorb onto TiO₂ without forming visible light absorbing surface complex. Another electron donating group t-Bu at the position 4 of catechol, CAT G, gave significantly low conversion of benzylamine. Apart from the electronic effect, very bulky t-Bu might play a role in preventing the interaction of catechol radical cation with TEMPO. Finally, we found that CAT D give the best results for the selective aerobic oxidation under blue LED irradiation. We will use it to carry on further investigation to the mechanistic insights of merging CAT D-TiO₂ complex photocatalysis with TEMPO for the visible-light-induced selective aerobic oxidation of benzylamine. The selective aerobic oxidation of benzylamines into imines on TiO₂ under UV irradiation was reported previously.25 Here, the reaction was achieved in higher concentration of amines, higher selectivities for imine products, much shorter reaction time and under milder irradiation of visible light and quite different reaction mechanism.

The formation of catechol-TiO₂ complex through bidentate mononuclear linkage was unequivocal according to ATR-FTIR and UV-visible absorbance (Figures S1 and S2). This mode of adsorption of catechol on anatase TiO₂ nanoparticles has been directly evidenced by combined solid state NMR and DFT calculation.²⁶ Moreover, there is little difference between CAT A- and CAT D-TiO₂ complexes. Benzylamine, TEMPO, CAT A, and CAT D does not absorb any visible light, implying catechol-TiO₂ complex was an authentic visible-light photocatalyst (Figure S3). We subtracted the absorption of TiO₂ to get visible light absorption of the surface complex (Figure S3, a) which is in significant overlap with the light emitting spectrum of blue LED (Figure S3, b), giving credence to the second-best results amongst the LEDs tested (Table S1). Next, we performed a plethora of control experiments to elucidate the nature of the selective aerobic oxidation (Table S2). It was found that CAT D, TiO₂ and TEMPO is an integral component of the visible light photocatalysis. Without one, two or three of them, the reaction can be stopped or significantly hampered (entries 1-7, Table S2). Benzylamine can directly form surface complex with TiO₂ that can lead to self-catalyzation under λ >420 nm visible light irradiation.²⁷ However, the control experiments unequivocally suggests that reaction induced by the surface complexation between benzylamine and TiO₂ (entry 1 vs. entry 2, Table S2) but induced by catechol-TiO₂ complex photocatalyst under blue LED irradiation. Besides, none of the individual component can absorb visible light (Figure S4). Without light irradiation, the reaction stopped (entries 8, Table S2), suggesting it is a true photocatalytic reaction. Control experiments regarding the nature reactive oxygen species indicated that superoxide but not singlet oxygen was involved in affording the imine product (entries 9-12, Table S2). Furthermore, we thoroughly studied the impact of the initial O₂ pressure and found that it had moderate influence on the aerobic oxidation of

benzylamine (Table S3). Therefore, atmosphere O₂ was an ideal oxidant in the present system for the visible-light-induced selective oxidation of benzylamine.

The reaction proceeded well in different inert organic solvents (Table S4); TiO₂ was of great importance in prompting the oxidation reaction (Table S5). These results suggest that the reaction conditions are quite general and further proves TiO₂ is an integral component of the complex as a photocatalyst. With the replacing of the anatase TiO₂, with rutile and Aeroxide P25 TiO₂, 1% and 19% conversions of benzylamine were obtained in 45 min, much inferior to that of the anatase TiO₂. Next, we carried out a battery of kinetics studies to shed more light on the reaction mechanism. It was uncovered that the visible-light-induced selective oxidation of benzylamine follows zero-order reaction (Figure 1, a), with a reaction rate constant k_H of 0.00525 mol·L⁻¹·min⁻¹. The oxidation of benzyl- α , α -d₂-amine conforms to the same reaction order and a reaction rate constant k_D of was obtained as 0.00261 mol·L⁻¹·min⁻¹. Thus, the kinetics isotope effect value k_{H}/k_{D} is 2.01, suggesting the C_a-H abstraction by TEMPO partially be involved in the rate determining step. To determine the nature of benzylamine radical after abstraction of C_{α} -H, Hammett plot for the oxidation kinetics of para-substituted benzylamines (Figure S5) was retrieved by correlating the electronic effect of para-substituted groups with log (k_X/k_H) to get an almost flat linear relationship (Figure 1, a), suggesting a neutral free radical participated in the reaction processes.



Figure 1. Reaction kinetics studies on merging the visible light photocatalysis of **CAT D**-TiO₂ complex with TEMPO using air as the oxidant (a) the selective oxidation of benzylamine (a); (b) the selective oxidation of benzyl- α , α -d₂-amine; (c) Hammett plot for the oxidation of *para*-substituted benzylamines. (a) 0.3 mmol of benzylamine, (b) 0.3 mmol of benzyl- α , α -d₂-amine, (c) 0.3 mmol of *para*-substituted benzylamine. Reaction conditions: 2.4×10⁻³mmol of **CAT D**, 50 mg of TiO₂, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL CH₃CN.

Without adding TEMPO into the photocatalytic system, we do observe *N*-centered free radical with ESR, indicating N radical cations was involved in the product formation. However, after adding TEMPO, the reaction pathways shifted divergently. TEMPO was intensively studied for the oxidation of alcohols. The application of it in the oxidation of amines was quite exiguous. Only several reports appeared in literature such as selective aerobic oxidation of primary amines to imines^{28, 29}, oximes³⁰ and nitriles³¹ with TEMPO and a transition metal catalyst. We previously disclosed the cooperative photocatalysis of dye-sensitized TiO₂ and TEMPO for visible-light-induced selective aerobic oxidation of amines to imines to imines can be viewed as an analogue for oxidation of alcohols,³³ offering new perspective for mechanistic implications. To further distinguish the role of TEMPO in the

View Article Online DOI: 10.1039/C8CY01096J

photocatalytic process, we used TEMPO as a stoichiometric oxidant after replacing the atmosphere O_2 with N_2 . Indeed, we found that imine can be afforded accompanied by generation of TEMPOH as the other product (eq. 2). TEMPOH can be rapidly re-oxidized back to TEMPO by superoxide $(O_2 \cdot \bar{})$, a well-accepted practice in biological or chemical studies.^{34, 35} By the same token, we hypothesized that the same catalytic amount of TEMPOH should be considered the equivalent of TEMPO. Thus, we used 5 mol% of TEMPOH to start out the investigation for the visible-light-induced aerobic oxidation of benzylamine and found almost the same results as TEMPO as the starting agent (eq. 3).



Based on the results above mentioned results including condition screenings, control experiments, kinetics studies, etc., a plausible reaction mechanism has been proposed in Figure 2. **CAT D** belongs to type II sensitizer during the electron injecting to the conduction band of anatase TiO₂. In addition, this type of sensitizer can lead to new broad absorption, accounting for all the visible light absorption in the present case. In this fashion, **CAT D** surface complex does not experience the excited state but rather directly injects electron to the conduction band of TiO₂ under blue LED irradiation. Simultaneously, radical cation will be generated at the **CAT D** surface complex which is under oxidative stress that need to be quickly released to safeguard its integrality.

View Article Online DOI: 10.1039/C8CY01096J



Figure 2. Plausible mechanism for the visible-light-induced selective aerobic oxidation of amines by catechol-TiO₂ complex photocatalysis merged with TEMPO

Hence, the catalytic cycle of TEMPO plays a such pivotal role in quenching the radical cation state of **CAT D** surface complex to refurbish its ground state. TEMPO⁺ will be created to commence the oxidation of benzylamine, producing benzylamine radical whose deprotonation resulting in the formation of benzaldimine. Before adding TEMPO, the mechanism should be quite similar to Au₂₅/TiO₂ photocatalyst in which the formation of imine is governed by single electron transfer.³⁶ We could use ESR to track the presence of N-centered free radicals (Figure S6). In contrast, with the involvement TEMPO, direct two-electron transfer pathway takes control of the oxidation of amine. The coupling between benzaldimine and benzylamine. In our previous report for the photocatalytic aerobic oxidation of sulfides, TEMPO was reestablished from TEMPO⁺. ³⁷ Currently, C_a-H of benzylamine was involved, resulting in the formation of TEMPOH which will be restore to TEMPO by O₂·⁻ formed by the reduction of O₂ by conduction band electron.

View Article Online DOI: 10.1039/C8CY01096J



Figure 3. The ESR spectra recorded during the selective oxidaiton of benzylamine by **CAT D**-TiO₂ photocatalysis (a) spin trapping of superoxide radicals (O_2^{-}) with DMPO (5,5-dimethyl-1pyrroline N-oxide), (b) TEMPO

We have confirmed that singlet oxygen was of negligent involvement but O_2 .⁻ was an overwhelmingly critical factor in the formation of imine through control experiments of using CD₃CN as a solvent and *p*-BQ quenching. To support this argument in a further step, we adopted *in situ* ESR technique to verify the free radicals that got involved in the reaction process (Figure 3). We can clearly observe the characteristics of DMPO trapped O_2 .⁻ and the signal increased with the progress of time (Figure 3, a), indicating the accumulation of DMPO trapped O_2 .⁻. Thus, it was constantly produced during the visible-light-induced photocatalytic process. Because TEMPO is an ESR active specie, we followed the signal of it during the progress of reaction. The ESR signal persists in the 10 min of irradiation, but the strength of the signal decreased (Figure 3, b), suggesting it was in part transformed into ESR inactive species, in agreement with the proposed mechanism in Figure 2.

Table 3. Visible-light-induced selective oxidation of amines into imines with air by **CAT D**-TiO₂ complex photocatalysis merged with TEMPO ^[a]



Entry	Substrate	Product	T(h)	Conv. [%] ^[b]	Sel. [%]
1	NH ₂	N C	1.2	98	98
2 ^[c]	NH ₂		3.5	95	98
3	MeO NH2	MeO	1.0	95	98
4	Me NH ₂	Me	1.0	98	97
5	t-Bu NH2	t-Bu	1.0	90	97
6	F NH2	F	1.0	92	98
7	CI NH2	CI N CI	1.0	90	96
8	Br NH ₂	Br	1.0	90	95
9	MeONH2	Meo OMe	1.0	90	97
10	OMe NH ₂	OMe OMe	1.5	94	98
11	NH ₂		1.5	97	96
12	N NH ₂		1.2	94	92
13	NH ₂	N S	1.5	91	97

[a] Reaction conditions: 0.3 mmol of primary amine, 2.4×10^{-3} mmol of **CAT D**, 50 mg of TiO₂, 0.015 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH₃CN. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of amine, selectivity of corresponding imine. [c] 1.2 mmol of primary amine, 4.8×10^{-3} mmol of **CAT D**, 100 mg of TiO₂, 0.06 mmol of TEMPO, 3 W blue LED irradiation, 1 mL of CH₃CN, 3.5 h.

After the clarification of mechanistic insights, we then evaluated a series of primary amines to probe the reaction scope and to generate preliminary information to further verify the mechanism (eq. 4). The scope for the selective aerobic oxidation of primary amines by merging the visible light photocatalysis of CAT D-TiO₂ complex (PXRD characterization, see Figure S7) and TEMPO was listed in Table 3. We first demonstrated that our reaction system can be carried out in very high concentration of amine and scaled up to the gram level of imine product (entry 1, Table 3). The CAT D-TiO₂ complex photocatalyst was recycled. And 80% yield for Nbenzylidenebenzylamine was achieved with adding CAT D. Importantly, we increased benzylamine and TEMPO catalyst to 4 times and CAT D-TiO₂ complex to twice, 0.103 g of Nbenzylidenebenzylamine can be afforded as 88% yield of imine product (entry 2, Table 3) in which the initial concentration of benzylamine is $1.2 \text{ mol} \cdot \text{L}^{-1}$ and turnover number in terms of CAT D is 250, quite remarkable results for photocatalysis based on TiO2. Para-substituted benzylamines with electron-donating or electron-withdrawing substitutes underwent the selective oxidation into imines with air with high conversions and selectivities (entries 3-8, Table 3). Importantly, the needed time to achieve comparable conversions for these different benzylamines were almost the same which is in agreement with the Hammett plot result and the proposed mechanism. This reaction pattern holds for the oxidation of *meta*-substituted benzylamine (entry 9, Table 3) and breaks for ortho-substituted benzylamine (entry 10, Table 3) in which longer time was needed. We

attributed this effect to the steric hindrance of the substitutes during the interaction with **CAT D** surface complex or TEMPO. Di-substituted benzylamine (entry 11, Table 3) also needed longer time to finish the oxidation reaction. Heteroatomatic methylamines such as 2-pyridinemethylamine and 2-thiophenemethylamine underwent the visible light photocatalytic aerobic oxidation into imines effectively (entries 12 and 13, Table 3).

4. Conclusion

Published on 03 July 2018. Downloaded by University of Michigan, Flint on 7/3/2018 10:11:27 AM.

In summary, we have developed a visible light photocatalyst system based on the catechol surface complexed TiO₂ for the selective oxidation of amines into imines with air with the guidance many years of fundamental research of the interfacial interaction between catechol and TiO₂. The key to our success is the merging the catechol-TiO₂ complex photocatalysis with TEMPO catalysis to make the photocatalyst durable under aerobic oxidative conditions and blue LED irradiation. We found that O_2 ·⁻ was essential reactive oxygen species in the oxidation process. Moreover, the degradation role of O_2 ·⁻ could be sufficiently contained by TEMPOH to regenerate TEMPO which in turn results in high selectivities for imine products through the orchestration of the photocatalytic and catalytic cycles.

Acknowledgment

Financial support from the National Natural Science Foundation of China (grant numbers 21503086 and 21773173), the Fundamental Research Funds for the Central Universities (grant number 2042018kf0212) and the start-up fund of Wuhan University is gratefully acknowledged.

References

- X. J. Lang, W. H. Ma, C. C. Chen, H. W. Ji and J. C. Zhao, Acc. Chem. Res., 2014, 47, 355-363.
- V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, J. Soria and S. Yurdakal, J. Phys. Chem. Lett., 2015, 6, 1968-1981.
- J. Schneider, M. Matsuoka, M. Takeuchi, J. L. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, *Chem. Rev.*, 2014, **114**, 9919-9986.
- R. Rodriguez, M. A. Blesa and A. E. Regazzoni, J. Colloid Interface Sci., 1996, 177, 122-131.
- 5. L. Gundlach, R. Ernstorfer and F. Willig, Phys. Rev. B, 2006, 74, 035324.
- 6. Y. Xu, W. K. Chen, S. H. Liu, M. J. Cao and J. Q. Li, Chem. Phys., 2007, 331, 275-282.
- R. Sánchez-de-Armas, M. A. San-Miguel, J. Oviedo, A. Márquez and J. F. Sanz, *Phys. Chem. Chem. Phys.*, 2011, 13, 1506-1514.
- 8. S. C. Li, L. N. Chu, X. Q. Gong and U. Diebold, Science, 2010, 328, 882-884.
- S. Higashimoto, T. Nishi, M. Yasukawa, M. Azuma, Y. Sakata and H. Kobayashi, J. Catal., 2015, 329, 286-290.
- K. L. Orchard, D. Hojo, K. P. Sokol, M. J. Chan, N. Asao, T. Adschiri and E. Reisner, *Chem. Commun.*, 2017, **53**, 12638-12641.
- P. Karthik, R. Vinoth, P. Selvam, E. Balaraman, M. Navaneethan, Y. Hayakawa and B. Neppolian, J. Mater. Chem. A., 2017, 5, 384-396.
- 12. Z. Tachan, I. Hod and A. Zaban, Adv. Energy Mater., 2014, 4, 1301249.
- 13. A. E. Wendlandt and S. S. Stahl, Angew. Chem. Int. Ed., 2015, 54, 14638-14658.
- 14. M. Largeron and M. B. Fleury, Angew. Chem. Int. Ed., 2012, 51, 5409-5412.
- 15. T. Tachikawa, Y. Takai, S. Tojo, M. Fujitsuka and T. Majima, Langmuir, 2006, 22, 893-896.

- 16. P. Jacobson, S. C. Li, C. Wang and U. Diebold, J. Vac. Sci. Technol. B, 2008, 26, 2236-2240.
- 17. L. Ye and Z. H. Li, ChemCatChem, 2014, 6, 2540-2543.
- 18. D. R. Sun, L. Ye and Z. H. Li, Appl. Catal., B, 2015, 164, 428-432.
- 19. M. Largeron and M. B. Fleury, Science, 2013, 339, 43-44.

- 20. X. J. Lang and J. C. Zhao, Chem. Asian J., 2018, 13, 599-613.
- 21. X. J. Lang, J. C. Zhao and X. D. Chen, Chem. Soc. Rev., 2016, 45, 3026-3038.
- W. Y. Zhang, E. Fernández-Fueyo, Y. Ni, M. van Schie, J. Gacs, R. Renirie, R. Wever, F. G. Mutti, D. Rother, M. Alcalde and F. Hollmann, *Nat. Catal.*, 2018, 1, 55-62.
- S. Kaniyankandy, S. Rawalekar, A. Sen, B. Ganguly and H. N. Ghosh, *J. Phys. Chem. C*, 2012, **116**, 98-103.
- J. Yang, Z. H. Wen, X. X. Shen, J. Dai, Y. Li and Y. J. Li, *Chem. Eng. J.*, 2018, 334, 907-921.
- X. J. Lang, H. W. Ji, C. C. Chen, W. H. Ma and J. C. Zhao, *Angew. Chem. Int. Ed.*, 2011, 50, 3934-3937.
- D. Finkelstein-Shapiro, S. K. Davidowski, P. B. Lee, C. Guo, G. P. Holland, T. Rajh, K. A. Gray, J. L. Yarger and M. Calatayud, *J. Phys. Chem. C*, 2016, **120**, 23625-23630.
- 27. X. J. Lang, W. H. Ma, Y. B. Zhao, C. C. Chen, H. W. Ji and J. C. Zhao, *Chem. Eur. J.*, 2012, 18, 2624-2631.
- 28. Z. Z. Hu and F. M. Kerton, Org. Biomol. Chem., 2012, 10, 1618-1624.
- B. Huang, H. W. Tian, S. S. Lin, M. H. Xie, X. C. Yu and Q. Xu, *Tetrahedron Lett.*, 2013, 54, 2861-2864.
- 30. J. T. Yu, X. H. Cao and M. Lu, Tetrahedron Lett., 2014, 55, 5751-5755.

- X. T. Ma, H. Xu, Y. L. Xiao, C. L. Su, J. P. Liu and Q. Xu, *Chin. Chem. Lett.*, 2017, 28, 1336-1339.
- 32. Z. Wang and X. J. Lang, Appl. Catal., B, 2018, 224, 404-409.
- 33. Y. C. Zhang, Z. Wang and X. J. Lang, Catal. Sci. Technol., 2017, 7, 4955-4963.
- S. I. Dikalov, I. A. Kirilyuk, M. Voinov and I. A. Grigor'ev, *Free Radical Res.*, 2011, 45, 417-430.
- A. Samuni, C. M. Krishna, J. B. Mitchell, C. R. Collins and A. Russo, *Free Radical Res. Commun.*, 1990, 9, 241-249.
- H. J. Chen, C. Liu, M. Wang, C. F. Zhang, N. C. Luo, Y. H. Wang, H. Abroshan, G. Li and F. Wang, ACS Catal., 2017, 7, 3632-3638.
- 37. X. J. Lang, J. C. Zhao and X. D. Chen, Angew. Chem. Int. Ed., 2016, 55, 4697-4700.

Table of contents entry

Merging the catechol- TiO_2 complex photocatalysis with TEMPO catalysis can successfully implement the selective oxidation of amines into imines with air under blue LED irradiation.

