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Photocatalytic organic transformation by layered double hydroxides: highly efficient and selective oxidation of primary aromatic amines to their imines under ambient aerobic conditions†

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We report the first application of layered double hydroxide as a photocatalyst in the transformation of primary aromatic amines to their corresponding imines with high efficiency and selectivity by using oxygen in an air atmosphere as a terminal oxidant under light irradiation.

Imine derivatives represent important intermediates for the synthesis of dyes, pharmaceuticals, agrochemicals and agricultural chemicals.[1] Over the past decades, a great deal of efforts have been made to develop mild and practical oxidation reactions for imine preparation.[2] Whereas the traditional condensation of aldehydes and amines has been well-established, direct oxidation of amines to imines is of intense current interest.[3] In particular, the use of light and molecular oxygen to trigger the conversion of amines to imines has aroused much attention.[4] For instance, Che *et al.*[4a] reported that a variety of secondary aromatic amines could be oxidized to imines in 90% to >99% yields using singlet oxygen generated from oxygen and a porphyrin photosensitizer. Wang and Blechert[4b] presented the aerobic oxidation of amines into imines in excellent yields by a mesoporous graphite carbon nitrile (mpg-C_3N_4) photocatalyst. Zhao *et al.*[4c] found a series of aromatic amines being transformed into the corresponding imines under light irradiation, air and TiO_2 in acetonitrile. Despite the fact that considerable efficient methods have been developed for the oxidation of secondary amines to imines, little attention has been given to the oxidation of primary amines until recently,[2] probably because the generated imines are intermediate products that are easily dehydrogenated to nitriles.

In this communication, we wish to report a highly efficient and selective oxidation of primary aromatic amines to imines using layered double hydroxide (LDH) as a photocatalyst and oxygen in air as an oxidant. Ruthenium(II),[5a,b] iridium(III),[5b,c] platinum(II),[5d] gold(II)[5e] complexes as well as organic dyes including eosin Y,[5f–h] rose bengal, and Bodipy[5i] have been involved in the photocatalytic reactions. However, the cost and stability of metal complexes and organic dyes in the course of irradiation remain a significant challenge. LDHs are well known as hydrotalcite-like materials with a general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}yH_2O$, where M^{II} and M^{III} are divalent and trivalent metals and A^{n-} is the exchangeable organic or inorganic anion.[6] The attractive advantages of LDHs are: (1) they can be prepared in large quantities in a reliable and reproducible manner by precipitation of an aqueous solution of the corresponding metal salts; and (2) the atomic ratio between the divalent and trivalent metal ions of the double layer can be varied over a wide range without altering the structure of the material. LDHs, particularly those bearing carbonate (CO_3^{2-}) as a compensating anion in the layers, have been widely used as supports and/or confined reaction space,[7a–c] and even as catalysts[7d–h] for hydrogenation[7d,e] and oxidation[7f] reactions. However, few examples have been reported on the photocatalytic organic transformation by LDHs. In 2009, García and coworkers[8] found that Zn^{II}/Ti^{IV}, Zn^{II}/Ce^{IV} and Zn^{II}/Cr^{III} LDHs at different Zn^{II}/metal atomic ratios of LDHs have the ability to generate oxygen through photocatalytic water splitting. Since then, the use of LDHs for photocatalytic hydrogen and oxygen evolution,[9a–e] carbon dioxide reduction,[9f,g] and even organic pollutant degradation,[9h] has been developed. Here, we present our findings for the first time on the highly efficient and selective photocatalytic oxidation of primary aromatic amines to imines by LDHs (Scheme 1). With light irradiation for 5 h, a simple, clean, recyclable and efficient method is established for the virtually quantitative and selective conversion of a variety of primary aromatic amines to their imines under ambient aerobic conditions.

Considering the enhanced performance in energy conversion,[9a] (Zn^{II}/Ti^{IV})LDH with a Zn^{II}/Ti^{IV} ratio of 6 : 1 is selected as

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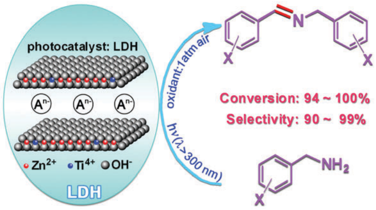


Scheme 1

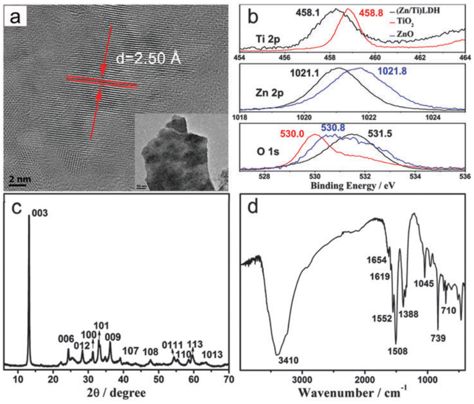
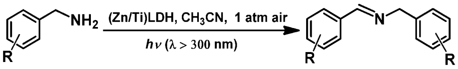


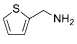
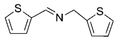
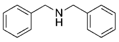
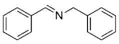
Fig. 1 (a) HR-TEM image and TEM image (inset), (b) XPS spectra, (c) powder XRD pattern, (d) FT-IR spectra of (Zn^{II}/Ti^{IV})LDH.

a photocatalyst, which was prepared according to the procedure in the literature.[8] High-resolution transmission electron microscopy (HR-TEM) images reveal that the (Zn^{II}/Ti^{IV})LDH has platelike structure, and the lattice fringe is single crystalline (Fig. 1a). X-ray photoelectron spectroscopy (XPS) shows the binding energy of Ti^{IV} $2p_{3/2}$ and Zn^{II} $2p_{3/2}$ in the (Zn^{II}/Ti^{IV})LDH shifted to the low energy as compared with that in TiO_2 and ZnO, respectively (Fig. 1b), indicating the specific interaction between Ti^{IV} and Zn^{II}. X-ray diffraction (XRD) study revealed long-range stacking order with the interplanar spacing of 2.5 Å (Fig. 1c). The absorption bands at 1654 cm^{-1}, 1619 cm^{-1}, 1508 cm^{-1}, 1388 cm^{-1} and 1045 cm^{-1} in fourier transform infrared (FT-IR) spectroscopy suggested the presence of the CO_3^{2-} anion, while bands between 500–900 cm^{-1} are due to the lattice M–O and M–OH vibration (Fig. 1d).

The photocatalytic aerobic oxidation was carried out at room temperature. 20 mg of (Zn^{II}/Ti^{IV})LDH was added into a 5 mL solution of acetonitrile and a primary aromatic amine such as benzylamine (0.2 mmol). The reaction mixture was then irradiated with a high-pressure mercury lamp (500 W) for 5 h under an air atmosphere. After irradiation, the product was isolated and identified by ^1H NMR spectroscopy. Control experiments showed that the photocatalyst (Zn^{II}/Ti^{IV})LDH, air and light were all essential for the effective oxidation of benzylamine (Table S2, ESI,† entries 1–4) and the transformation cannot proceed effectively in the absence of light. Notably, the photocatalytic activity of (Zn^{II}/Ti^{IV})LDH is better than TiO_2 (P25) and ZnO (Table S2, ESI,† entries 1, 5 and 6), possibly due to the enhanced electron–hole separation efficiency by superior dispersion of active TiO_6 units.[9e]

Table 1 Photocatalytic oxidation of aromatic amines[a]



Entry	Substrate	Product	t (h)	Conv.[b] (%)	Select.[b] (%)
1	R = H	R = H	5	100	97
2	R = *p*-Me	R = *p*-Me	5	99	97
3	R = *o*-OMe	R = *o*-OMe	5	96	99
4	R = *m*-OMe	R = *m*-OMe	5	99	93
5	R = *p*-OMe	R = *p*-OMe	5	98	96
6	R = *p*-F	R = *p*-F	5	100	95
7	R = *p*-Cl	R = *p*-Cl	5	98	91
8	R = 3,4-diCl	R = 3,4-diCl	5	99	91
9	R = *p*-Br	R = *p*-Br	5	94	90
10			8	99	99
11			8	93	96

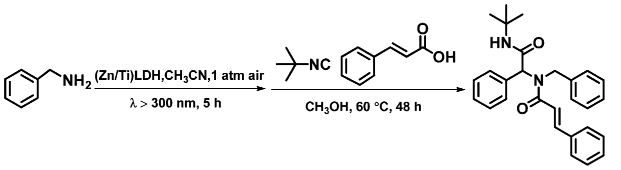
[a] Reaction conditions: 0.2 mmol substrate, 20 mg (Zn^{II}/Ti^{IV})LDH, 5 mL CH_3CN, 1 atm air, 500 W high pressure Hg lamp ($\lambda > 300$ nm). [b] Determined by ^1H NMR ($CDCl_3$) using 1,3,5-trimethoxybenzene as the internal standard.

To examine the composition effect on the photocatalytic reaction, (Zn^{II}/Ti^{IV})LDH with a Zn^{II}/Ti^{IV} ratio of 4 : 1 and 5 : 1, respectively, was also prepared. It was found that (Zn^{II}/Ti^{IV})LDH with a ratio of 6 : 1 shows the highest photocatalytic activity (Table S2, ESI,† entries 1, 7 and 8), which may be due to its higher crystallinity and purity than that of (Zn^{II}/Ti^{IV})LDH (5 : 1) and (Zn^{II}/Ti^{IV})LDH (4 : 1) (as indicated in the XRD patterns in Fig. S2, ESI†).[9e] In addition, the generality of LDHs as photocatalysts for the organic transformation was tested. We made a sample of traditional (Mg^{II}/Al^{III})LDH (Fig. S3, ESI†), and found that it enabled the photocatalytic oxidation of benzylamine smoothly in a good chemical yield (87%, Table S2, ESI,† entry 9).

As shown in Table 1, the protocol can be used to convert a broad range of primary aromatic amines into their corresponding imines leaving various substituents unaffected. Using (Zn^{II}/Ti^{IV})LDH as the photocatalyst and oxygen in air as the oxidant, good to excellent conversion and selectivity were obtained no matter electron-donating (entries 1–5) or electron-withdrawing (entries 6–9) groups were present on the benzene ring. When a heterocyclic compound, 2-thiophene methylamine, was used as a substrate, the aerobic oxidation conversion and efficiency of the photocatalyst are excellent.

In an effort to enhance the economic and environmental attractiveness of the method, the reusability of the photocatalyst was assessed. After work up of an irradiated sample with benzylamine as the substrate, the (Zn^{II}/Ti^{IV})LDH photocatalyst was separated from the liquid by centrifugation and reused for catalyzing the reaction of a second batch of benzylamine. Strikingly, the catalyst functioned as it did initially. After three additional runs with the same catalyst, a similar conversion and yield were achieved as in the first run (Fig. S4, ESI†).

Because LDHs are easy to isolate from the reaction system for the next cycle, we further examined the reactivity of imines generated *in situ* for the Ugi reaction.[4a,10] Zhu and coworkers[10] reported the first example of oxidative three-component Ugi-type

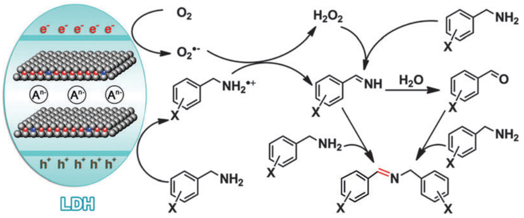


Scheme 2 One-pot synthesis of Ugi-type reaction starting from benzylamine.

reaction by oxidation of amines with singlet oxygen, a key step of which is the oxidation of benzylic amine to imine, followed by reaction of the imine with isocyanide and carboxylic acid. Che and coworkers[4a] used the *in situ* formed imine products from porphyrin and singlet oxygen for application in the Ugi-type reactions. Herein, the imine from primary benzylamine and oxygen in air, (Zn^{II}/Ti^{IV})LDH under light irradiation was refluxed with cinnamic acid and *t*-butylisocyanide in methanol to obtain the Ugi product in 82% yield (Scheme 2), which is comparable to those reported in the literature.[4a]

It is important to note that molecular oxygen is crucial for the transformation of primary aromatic amines to imines. When the reaction was performed in argon atmospheres, trace amounts of photoproduct could be detected (Table S2, ESI,† entry 3). It is accepted that singlet oxygen $(^1O_2)$[4a,5i] or the superoxide radical anion $(O_2^{-\bullet})$[4b,d] is responsible for the conversion of amines to imines. To figure out the active species of oxygen in the current study, superoxide dismutase (SOD, $O_2^{-\bullet}$ scavenger) was added to the photocatalytic aerobic oxidation system containing (Zn^{II}/Ti^{IV})LDH and benzylamine under an air atmosphere (this reaction was performed in water because SOD is insoluble in acetonitrile). The yield of reaction was found to decrease from 46% to 2% (Table S2, ESI,† entries 10 and 11), suggesting that $O_2^{-\bullet}$ plays a key role in the whole process. Moreover, upon introduction of starch/KI/CH_3COOH into the system after 1 h irradiation, the color of solution changed from white to dark purple (Fig. S5, ESI†), which provides evidence of the formation of H_2O_2 in the reaction system.

On the basis of the above results, a possible mechanism for the photocatalytic aerobic oxidation reaction (Scheme 3) could be speculated. Because of two different metals in LDH, it can be regarded as a kind of ''doped semiconductor''.[8,9] The band gap of (Zn^{II}/Ti^{IV})LDH was calculated to be about 3.2 eV from the UV-vis diffuse reflectance spectrum (Fig. S6, ESI†). Light irradiation of (Zn^{II}/Ti^{IV})LDH results in the promotion of electrons to the conductive band (CB), thereby leaving holes in the valence band (VB, Scheme 3). Oxygen is then reduced by the photogenerated electrons to form $O_2^{-\bullet}$ and benzylamine is simultaneously oxidized by the photogenerated hole. The generated $O_2^{-\bullet}$ abstracts a proton and a hydrogen atom from the benzylamine radical cation to form benzenemethanimine and H_2O_2. Successive addition of benzenemethanimine to another molecule of benzylamine gives rise to the target imine product. Meanwhile, the formed H_2O_2 intermediate can also react with the benzylamine substrate (Table S2, ESI,† entry 12), though the contribution of H_2O_2 to the reaction was proven to be minor in the reaction system (Table S2, ESI,† entries 13 and 14). A trace amount of benzaldehyde product could be detected in the acetonitrile solution owing to a small amount of H_2O formed. Nevertheless, the selectivity of the transformation of primary aromatic amines to imines approaches >99%.



Scheme 3 Possible benzylamine aerobic oxidation reaction pathways.

In summary, we have succeeded in the conversion of primary aromatic amines to their imines for the first time by using (Zn^{II}/Ti^{IV})LDH as a photocatalyst in the aerobic atmosphere. The (Zn^{II}/Ti^{IV})LDH photocatalyst is stable, effective, economical and reusable. In contrast to those reported in the literature, $O_2^{-\bullet}$ generated from (Zn^{II}/Ti^{IV})LDH and oxygen in air has been demonstrated to be responsible for the oxidation of aromatic amines to imines as well as the Ugi reaction. More interestingly, the (Zn^{II}/Ti^{IV})LDH enables the transformation of primary aromatic amines into their corresponding imines efficiently and selectively, whereas leaving the substituents unaffected. It is anticipated that the utilization of LDHs as photocatalysts would be useful for cleaner, safer and cheaper organic transformation.

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