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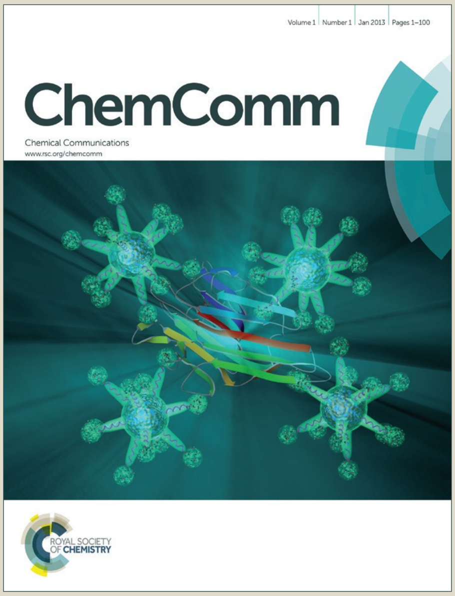

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A Green and Efficient Photocatalytic Route for High-Selective Oxidation of Saturated Alpha-Carbon C–H Bond in Aromatic Alkanes over Flower-like Bi_2WO_6

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A green and efficient route for high-selective oxidation of saturated alpha-carbon C-H bond in aromatic alkanes under visible-light irradiation and solvent-free condition is developed using flower-like Bi_2WO_6 microspheres as catalyst.

Among the oxidation reactions of hydrocarbon, the efficient and selective activation of saturated C-H bonds in alkanes or aromatics for the generation of value-added products such as aldehydes and ketones is a significant challenge both in organic synthesis and chemical industry.[1] Because of the low selectivity and/or conversion, the conventional processes are unsatisfactory. In addition, the systems are usually environment-unfriendly. Since the saturated C-H bonds are thermodynamically strong and dynamically inert, the reaction conditions are usually harsh, requiring high temperature, high pressure, and extra initiators or toxic reagents.[2-5] From the viewpoint of green chemistry, it is desirable to develop an environment-benign route that is highly efficient for the conversion of alkanes or aromatics to value-added products.

It was demonstrated that heterogeneous photocatalysis has huge potential in the oxidation of hydrocarbons.[6-10] So far, only a limited amount of catalysts, e.g. TiO_2 or TiO_2-based,[11-15] CdS or CdS-based materials,[16, 17] and Nb_2O_5,[18] were researched for the selective photo-oxidation of alkanes or aromatic alkanes using O_2 as oxidant. However, the application of these catalysts is hampered by ill factors such as low selectivity, poor efficiency, and the need of using ultraviolet light or organic solvents. As far as the use of visible light is concerned, the works on photocatalytic selective oxidation of alkanes or aromatic alkanes are rare, especially for those without the use of noxious solvents.[19, 20] Furthermore, for the few known cases there are shortcomings such as low selectivity, extra-initiator involvement, above room temperature (60°C) and use of noble metal. Hence, it is necessary to design high-efficiency photocatalysts for the oxidation of saturated C-H bonds. As a simple Aurivillius oxide, bismuth tungstate (Bi_2WO_6) shows good performance in the degradation of organic compounds under visible-light irradiation, owing to its suitable band location and unique layered structure.[21-25] The Bi_2WO_6 materials are low-cost and easily prepared. Recent reports demonstrated that Bi_2WO_6 exhibits appreciable results for the selective oxidation of alcohols under visible-light irradiation.[26-30]

Herein, we report for the first time the use of flower-like Bi_2WO_6 as photocatalyst for highly selective and efficient oxidation of aromatic alkanes using O_2 as oxidant under visible-light irradiation and solvent-free condition. We reveal the pivotal roles of photogenerated holes (h^+) and superoxide radicals, and propose a possible mechanism for the reaction.

The flower-like Bi_2WO_6 microspheres were prepared by a simple hydrothermal method, and the details are provided in the Electronic Supplementary Information (ESI).† According to the SEM images (Fig. 1a and b), the flower-like microspheres are 6-7 μm in diameter and are made up by nano-sheets. Based on the results of XRD and XPS analysis (Figure S1 and S2), the microspheres are identified as orthorhombic Bi_2WO_6.[31, 32]

In UV-Vis DRS study, the flower-like Bi_2WO_6 microspheres exhibit intense absorption in both ultraviolet and visible-light regions (Fig. 1d). The band gap energy (E_g) is estimated to be 2.96 eV based on the absorption spectrum and the $(Ah\nu)=K(h\nu-E_g)^n$ formula.[33] The calculated position of conduction and valence band is at -0.41 and 2.55 eV, respectively (Fig. S3), implying a relatively strong oxidation ability of the material. Since $H_2O/{\cdot}OH$ and $O_2/O_2^{\cdot-}$ display a standard redox potential (vs. NHE) of 2.3 and -0.28 eV that are within the redox capability of the flower-like Bi_2WO_6, the band structure provides the feasibility and theoretical basis for the formation of hydroxyl radicals (·OH) and superoxide radicals ($O_2^{\cdot-}$).

The selective oxidation of typical primary aromatic alkanes was carried out at room temperature in the absence of solvent over various catalysts under visible-light irradiation for 5 h. Under N_2 atmosphere or in the absence of a photocatalyst and/or light

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†Electronic Supplementary Information (ESI) available: experimental details, photocatalyst characterization figures, photocatalytic activity experiments. See DOI: 10.1039/x0xx00000x

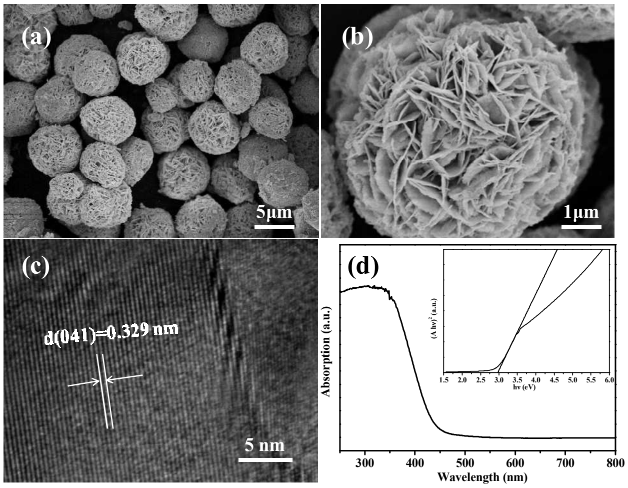


Fig. 1 (a-b) SEM images, (c) TEM image, and (d) UV-Vis DRS of flower-like Bi_2WO_6; the inset is the corresponding $(Ah\nu)^2$ versus photon energy plot

illumination, there is no detection of reactivity. The results of the control experiments suggest that the reaction is photocatalytic, and an oxidant such as O_2 is needed.

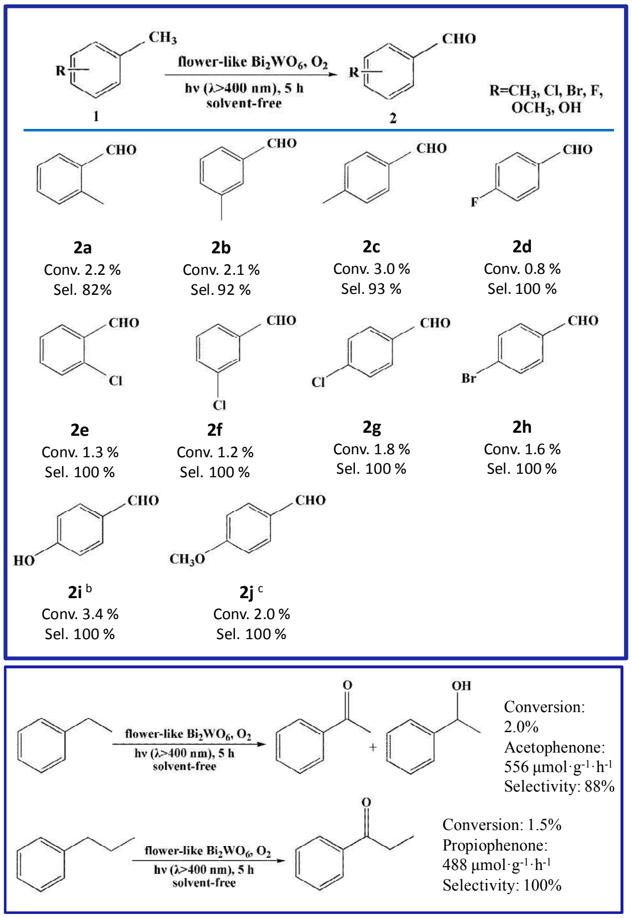
The photocatalytic activity of selective oxidation of toluene was examined over CdS [16] and Bi_2WO_6 of different morphologies [25, 34, 35] (prepared according to the reported literatures) (Table 1). It was observed that the flower-like Bi_2WO_6 performs the best, showing the highest reaction rate (464 μmol·g^{-1}·h^{-1}) and conversion (1.5%). The only by-product of the reaction is benzyl alcohol. Since all the prepared samples exhibit good response of visible light and the band gaps of Bi_2WO_6 with different morphologies are similar (Fig. S4), the high performance of flower-like Bi_2WO_6 is unlikely to be due to the good response of visible light or the appropriateness of band gap. Besides, the structure properties and photoluminescence (PL) results of the as-prepare Bi_2WO_6 samples (Fig. S5 and S6, and Table S1) do not suggest that the better photoactivity of flower-like Bi_2WO_6 can be ascribed to factors such as surface area, pore volume or separation ability of photogenerated charge carriers. Considering that the as-prepared Bi_2WO_6 samples are greatly different in morphology (Fig. S7), it is deduced that the high performance is ascribable to the unique flower-like structure of Bi_2WO_6, and the enhancement of visible light absorption as a result of multi-reflection of light across the structure.

Table 1 Selective oxidation of toluene over different photocatalysts under visible-light irradiation [a]

Catalyst	Benzaldehyde (μmol·g^{-1}·h^{-1})	Conv. (%)	Sel. (%)
CdS	240	0.7	98
Nanoparticle Bi_2WO_6	172	0.6	97
Nanoplate Bi_2WO_6	160	0.5	95
Nest-like Bi_2WO_6	140	0.4	96
Flower-like Bi_2WO_6	464	1.5	96

[a] Photocatalyst (50 mg), substrate (8 mmol), no solvent, room temperature, O_2 flow rate (3 mL·min^{-1}), visible-light irradiation (λ > 400 nm, 5 h).

Scheme 1 Substrate scope for photocatalytic oxidation of aromatic alkanes in this study [a]



[a] Substrate (8 mmol), catalyst (50 mg), O_2 flow rate (3 mL·min^{-1})

[b] P-cresol (8mmol), catalyst (50 mg), benzotrifluoride (2 mL), O_2 flow rate (3 mL·min^{-1})

[c] P-methoxytoluene (1 mmol), catalyst (50 mg), acetonitrile (2 mL), O_2 flow rate (3 mL·min^{-1})

It was found that the selective oxidation of toluene derivatives over flower-like Bi_2WO_6 is also effective (Scheme 1). It is noted that the oxidation of ethylbenzene or n-propylbenzene produces ketones rather than aldehydes. Thus, only the alpha-carbon of C-H bond is activated in this photocatalytic system. Compared with the oxidation of xylenes, the lower transformation of chlorotoluenes can be associated with the presence of electron withdrawing group (–Cl) that inhibits the oxidation activity of the methyl. That is, the methyl of xylenes is more active than that of chlorotoluenes. For the same reason, the selectivity to chlorobenzaldehydes is 100%,

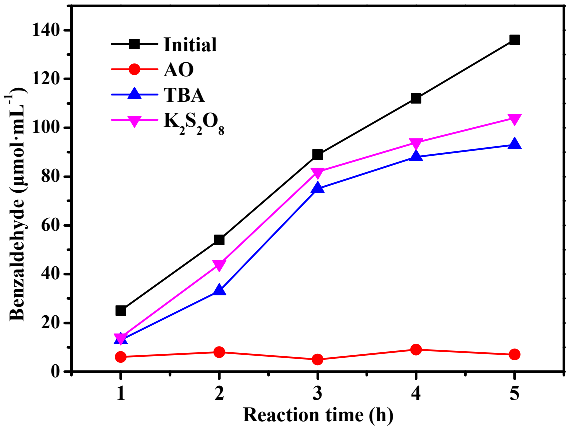


Fig. 2 Kinetic-experiments for selective oxidation of toluene under visible light in the presence or absence of various radical scavengers over flower-like Bi_2WO_6 (AO as hole scavenger, $K_2S_2O_8$ as electron scavenger, and TBA as hydroxyl radical scavenger).

whereas in the oxidation of xylenes, there is the generation of the corresponding alcohols as by-product.

Furthermore, time-dependent scale-up experiments on toluene oxidation over flower-like Bi_2WO_6 show that there is effective increase of benzaldehyde yield but no significant change of the high selectivity upon the extension of irradiation time (Fig. S8). With such performance, it is clear that the flower-like Bi_2WO_6 is a photocatalyst effective for the oxidation of aromatic alkanes to the corresponding aldehydes. In all cases of using flower-like Bi_2WO_6, there is no detection of carbon dioxide, indicating the absence of over oxidation during the photocatalytic processes.

We performed experiments to prove that the photocatalytic oxidation of toluene over Bi_2WO_6 involves free radicals. By adding 0.01 mmol tetra-methylpiperidine N-oxide (TEMPO) which is a typical radical scavenger, we quench the transformation of toluene to benzaldehyde almost completely. Furthermore, the effects of different active species in the reaction system were explored. Kinetic-experiments were performed with an appropriate amount of ammonium oxalate (AO), potassium persulphate ($K_2S_2O_8$) and *tert*-butanol (TBA) as scavenger for holes (h^+), photogenerated electrons (e^-) and hydroxyl radicals (·OH), respectively.[36-38] As shown in Fig. 2, the conversion of toluene is almost prohibited in the presence of AO, and there is no increase of conversion with reaction time. The results indicate that the holes are vital for the activation of toluene. Besides, both the addition of TBA and $K_2S_2O_8$ results in a certain decrease of toluene conversion. The results suggest that ·OH and e^- are also involved in the reaction, but their influences are apparently moderate. Since O_2 accepts photogenerated electrons easily to produce superoxide radical ($O_2^{\cdot-}$), [39] it was considered as oxidant for the transformation of toluene.[16] In this study, the conversion of toluene increase with time in the presence of electron scavenger $K_2S_2O_8$. In other words, the oxidation by $O_2^{\cdot-}$ is unlikely to occur or only plays a minute role in this system.

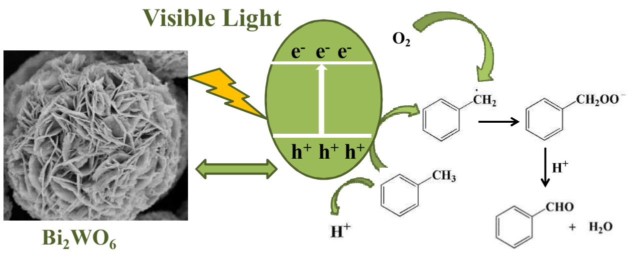


Fig. 3 Schematic of the plausible mechanism for photocatalytic selective oxidation of toluene to benzaldehyde over flower-like Bi_2WO_6 under visible-light irradiation

Based on the above results, it is deduced that the major active species for the photocatalytic selective oxidation of toluene is h^+ rather than ·OH or e^-. To a certain degree the deduction is in agreement with the active species commonly found in systems for the oxidation of hydrocarbons.[16, 27, 28] Accordingly, we propose a plausible mechanism for the catalytic reaction (Fig. 3). Before the start of visible light illumination, toluene gets in touch with Bi_2WO_6. After then, the photogenerated holes from valence band and electrons from conduction band are transferred to the Bi_2WO_6 surface under visible light irradiation. The direct oxidation of toluene for the formation of toluene cationic radicals as facilitated by the holes is a vital step. This step involves the activation of saturated C-H bond and is often regarded as the rate-determining step for selective oxidation of alkanes.[1] Finally, the O_2 dissolved in toluene combines with the toluene cationic radicals to generate the target product benzaldehyde. In this reaction system the holes play a key role in the direct dehydrogenation of toluene to the radical intermediate, and O_2 is the main oxidizing species.

In summary, a green and efficient system has been developed for the selective oxidation of aromatic alkanes into valuable products under mild conditions. This is the first report on the use of easily synthesized flower-like Bi_2WO_6 as active photocatalyst for the selective oxidation of aromatic alkanes under visible-light irradiation without the need of any solvents. The good performance of flower-like Bi_2WO_6 toward the oxidation of aromatic alkanes is attributed to its unique morphology. We investigated the specific functions of active intermediate species, and proved that the photogenerated holes are significantly involved in the oxidation process. A plausible reaction mechanism is proposed. The visible-light driven method using flower-like Bi_2WO_6 opens an environment-friendly way for efficient synthesis of organic compounds that requires the activation of saturated alpha-carbon C-H bonds.

This project was financially supported by NSFC (Grant nos. 21401054, 21476065), the China Postdoctoral Science Foundation (2014M562098) and the Fundamental Research Funds for the Central Universities. C.-T. Au thanks the Hunan University for an adjunct professorship.

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