Highly Selective Anaerobic Oxidation of Alcohols Over Fe-doped SrTiO$_3$ Under Visible Light

Yezi Hu,$^{[a]}$ Guixia Zhao,$^{[a, b]}$ Qiushi Pan,$^{[b]}$ Huihui Wang,$^{[a]}$ Zewen Shen,$^{[a]}$ Baoxiang Peng,$^{[b, c]}$ G. Wilma Busser,$^{[b]}$ Xiangke Wang,$^{[a]}$ and Martin Muhler$^{[b, c]}

Photocatalytic oxidation of alcohols with high selectivity is a promising approach for the synthesis of organic compounds under mild conditions and for solar energy conversion. In this work, we report on the highly selective anaerobic photocatalytic oxidation of alcohols to carbonyl compounds with coupled H$_2$ production over Pt-loaded Fe-doped SrTiO$_3$ under visible light. Representatively, an optimized apparent quantum efficiency of 13.2% at 420 nm was obtained for benzyl alcohol oxidation. X-ray absorption fine structure and in situ diffuse reflectance IR spectroscopy revealed that the surface oxygen vacancies and fine-tuned valence band edge position induced by Fe doping not only contributed to the activation of C–H bonds in alcohols, but also avoided the over-oxidation of the obtained carbonyl compounds. With optimized apparent quantum yields reaching 38%, 46% and 48% at 447 nm for the dehydrogenation of methanol, ethanol and 2-propanol, respectively.$^{[11]}$ Li et al. investigated the role of molecular catalysts in tuning the selectivity of photocatalytic transformation over a molecular Ru catalyst and Pt-modified g-C$_3$N$_4$ catalysts, revealing that the formation of a Ru (IV) = O intermediate dramatically improved the selectivity towards aldehydes.$^{[6]}$ Peroxoske oxides such as strontium titanate with stable photo-response are rarely studied in the photocatalytic oxidation of alcohols under anaerobic condition. Recently, we applied Rh-doped SrTiO$_3$ as photocatalyst in the anaerobic oxidation of alcohols under visible light, which was able to efficiently and selectively convert alcohols to carbonyl compounds. The apparent quantum efficiency (AQE) for the oxidation process of pure benzyl alcohol reached 49.5% at 420 nm.$^{[7]}$ It was found that the photocatalytic performance was highly dependent on the abundance of surface oxygen defects generated by doping with Rh. Due to the limited resources and the high price of Rh, more abundant elements such as Fe are considered promising to achieve selective photocatalytic oxidation of alcohols under visible light.$^{[8]}$ Fe-doped SrTiO$_3$ (Fe-STO) has not been widely studied as photocatalyst except for a few reports on photodegradation.$^{[9]}$ Herein, we synthesized Fe-doped SrTiO$_3$ with deposited Pt nanoparticles (NPs) acting as cocatalyst for the selective photocatalytic oxidation of alcohols under anaerobic condition. The alpha C–H bonds in the alcohol molecules were activated by the oxygen defects on the photocatalyst surface and the limited oxidation potential of Fe-doped SrTiO$_3$ with fine-tuned valence band edge contributed to the very high selectivity.

Results and Discussion

The highly crystalline Fe-doped SrTiO$_3$ nanoparticles were synthesized by the polymerized complex method and exhibited a cubic phase of SrTiO$_3$ when calcined higher than 500°C.$^{[10]}$ Fe can be detected by XPS as shown in Figure S2. The Fe 2p$_{3/2}$
amounts of Fe in STO calcined at 600°C (ICP); b) amounts of produced benzaldehyde over different initial doping distances observed for the SrTiO$_3$ particles sized between 20 and 30 nm. The lattice binding energy of 710.5 eV and the spin-orbit splitting of 13.6 eV confirm the +3 oxidation state of the Fe ions. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images of Pt-loaded Fe-STO-600 (Figures 1c and 1d) indicate that the smaller Pt NPs with diameters of about 4 nm were deposited homogeneously on the larger Fe-doped SrTiO$_3$ particles sized between 20 and 30 nm. The lattice distances observed for the SrTiO$_3$ and Pt NPs were 0.272 and 0.224 nm, corresponding well to the (111) lattice plane of SrTiO$_3$ and to the (111) lattice plane of face-centered cubic Pt, respectively. The specific surface area derived from the N$_2$ adsorption-desorption isotherms (Figure S3) of Fe-STO-600 was 31.1 m$^2$/g, smaller than that of Fe-STO-500 (38.2 m$^2$/g) due to the larger particle size. The impact of Fe doping on the optical response of the Fe-STO samples was evaluated by UV-vis spectroscopy (Figure 1b). The absorption edge positions of all the Fe-STO samples were shifted towards the visible light region compared with that of the undoped STO sample. The absorption tail extending from UV to about 600 nm is mainly attributed to the electron excitation from the impurity energy level in the forbidden band of SrTiO$_3$, which was created by the introduction of the Fe ions. Accordingly, with increasing calcination temperature the color of the materials (Figure S4) continuously deepened towards the brownish yellow color of Fe-STO-900. In addition, the valence band maxima (VBM) of STO and Fe-STO-600 were located at 2.27 eV and 1.87 eV (vs. NHE), respectively, according to XPS VB results (Figure S5), indicating that Fe doping lowers the oxidation potential of the photo-generated holes.

The performance in visible-light photocatalytic anaerobic oxidation of benzyl alcohol (BA) in saturated aqueous solution was evaluated by optimizing the calcination temperature, the amount of doped Fe, and the amount of loaded Pt. The results shown in Figure 2 indicate that the most active catalyst was 3 mol% Fe-STO-600 (with 3.00 mol% doping amount of Fe) loaded with 3.26 wt% Pt (with 4 wt% initial loading amount of Pt), yielding 130.3 μmol of benzaldehyde under 6 h irradiation with very high selectivity. The AQE at 420 nm determined with pure benzyl alcohol was 13.2%. Figure 3a displays the amounts of produced benzaldehyde as a function of time in the saturated aqueous benzyl alcohol solution. The production of benzaldehyde in the first 10 min was 59.8 μmol, while the corresponding benzaldehyde yield after 6 h was 129.7 μmol, indicating that the production rates decreased as a function of time during a single test, while the benzaldehyde yield showed no obvious variation for five recycle tests, indicating stable photocatalytic performance. Hence, the decrease of the production rates may be caused by the decreasing desorption rate of products from the catalyst with increasing product concentration in solution. The coupled H$_2$ evolution was confirmed by the GC-based analysis of the gas phase (Figure S6).
and amounted to 126.3 μmol after 6 h implying stoichiometric H₂ evolution and benzaldehyde production.

In order to identify the reactive species, ammonium oxalate, benzoquinone and tert-butyl alcohol were added to the reaction solution as hole, electron and hydroxyl radical scavengers, respectively. Figure 2d shows that photogenerated holes play a dominant role in the oxidation process, while both electrons and hydroxyl radicals were not the relevant reactive species, suggesting the absence of aggressive radical species in the reaction, which explains the high selectivity to the aldehyde.

The photocatalytic activities for various aromatic and aliphatic alcohols were also investigated to demonstrate the broad scope of the Pt-loaded Fe-STO-600 photocatalyst (Table 1). Although the degrees of conversion of substrates with varying substituent groups are different, all the derived selectivities were close to 100%, even for cinnamyl alcohol. The limited oxidation potential of the catalyst prevented water from being oxidized to hydroxyl radicals, and the anaerobic reaction formation, thus ensuring the high selectivity.

From the charge balance point of view, Fe³⁺ substituting Ti⁴⁺ would generate oxygen vacancies (OV) in the SrTiO₃ lattice. Thus, electron paramagnetic resonance (EPR) spectroscopy was applied to identify their presence. The room temperature EPR signal (Figure 4a) at approximately g = 2.008 for pristine STO samples can be assigned to natural surface oxygen vacancies formed during calcination,[16] while for the Fe-STO samples, an additional sharper signal with significantly higher intensity centered at g = 1.993 can be assigned to Ti³⁺ in the lattice,[17] indicating that the substitution of Ti⁴⁺ by Fe³⁺ induced Ti³⁺ in the lattice. It is interesting to note that the intensity of this Ti³⁺ signal reaches its maximum when the doping amount is 3 mol%, matching well with the optimized photocatalytic performance. Thus, Ti³⁺/OVs play an important role in the photooxidation of alcohols, as the presence of Ti³⁺ signals detected at room temperature is indicative for the presence of OVs.[18] The EPR signals of surface oxygen vacancies and Ti³⁺ were less intense after loading of Pt, maybe due to the electron transferring from Ti³⁺/OVs to the Pt NPs. In the EPR spectra measured at 77 K (Figures 4b and 4c), the signals at around g = 1.993 and g = 2.008 can be ascribed to Ti³⁺ and surface oxygen vacancies, respectively, which is consistent with the results obtained at room temperature. According to literature, Fe³⁺ ions exhibit two signals at g ~ 4.3 and g ~ 2, assigned to high-spin Fe³⁺ in a strong crystal field of complete rhombic distortion from octahedral symmetry and cubic Fe³⁺ with isotropic −1/2 → +1/2 transition, respectively.[19] A broadened EPR signal near g ~ 4.301 (Figure 4b) was found in Fe-STO-600, but the signal at g ~ 2 is assumed to be overlapped by the signal at g = 2.008.

We used extended X-ray absorption fine structure (EXAFS) to analyze the coordination of the Ti and Fe ions in Fe-doped SrTiO₃. Figures 5a–5c show the X-ray absorption spectra recorded for the STO and Fe-STO-600 samples at the Ti K-edge and Fe K-edge. The Fe K-edge X-ray absorption near edge structure (XANES) signals (Figure 5d) with a pre-edge peak at 7113 eV demonstrate that iron is present as Fe³⁺ after annealing in air, which is consistent with the XPS results.[20] The structural parameters derived from the Ti K-edge EXAFS data analyses are summarized in Table 2. The first peak arises from the Ti–O shell with a distance of 1.95 Å, and the second peak originates from the Ti–Sr shell with a distance of 3.35 Å in the Fe-STO-600 sample (Figures 5e and 5f). The Ti–O coordination number in reference SrTiO₃ was found to be 6, confirming perfect coordination.[20] For the Fe-doped SrTiO₃ sample, the coordination number was about 5.6, reflecting the formation of oxygen vacancies in the first shell due to Fe doping in the lattice.[21] The EXAFS fitting results show that the mean Fe–O

![Figure 4: EPR spectra and crystal structure](image)

**Figure 4.** a) Room temperature EPR spectra of STO and Fe-STO samples doped with different amounts of Fe; b) EPR spectrum of Fe-STO-600 sample measured at 77 K; c) details of EPR spectrum around g ~ 2 for Fe-STO-600 sample measured at 77 K; d) crystal structure of Fe-STO, showing the OV position in the first coordination spheres.

| Entry | Alcohol       | Product       | Con. [%] | Sel. [%] |
|-------|---------------|---------------|----------|----------|
| 1     | benzyl alcohol| benzaldehyde  | 30       | >99      |
| 2     | 2-methylbenzyl alcohol| 2-meth-ylbenzaldehyde | 32       | >99      |
| 3     | 4-methylbenzyl alcohol| 4-meth-ylbenzaldehyde | 53       | >99      |
| 4     | 2-chlorobenzyl alcohol| 2-chlorobenzaldehyde | 94       | >99      |
| 5     | 4-chlorobenzyl alcohol| 4-chlorobenzaldehyde | 83       | >99      |
| 6     | cinnamyl alcohol| cinnamyl aldehyde | 42       | >99      |
| 7     | 2-propanol    | acetone       | 13       | >99      |
| 8     | ethanol       | acetaldehyde  | 5        | >99      |

(a) Reaction conditions: 0.3 mmol reactant and 100 mg catalyst (3.26 % Pt/3.00 % Fe-STO-600) in 15 mL water in Ar atmosphere under visible-light (300 W Xe lamp, λ > 400 nm) irradiation for 6 h at 15°C.

**Table 1. Photocatalytic oxidation of a series of alcohols in aqueous solution.**

- Ti³⁺ signals in a strong crystal field of complete rhombic distortion from octahedral symmetry and cubic Fe³⁺ with isotropic −1/2 → +1/2 transition, respectively.[19] A broadened EPR signal near g ~ 4.301 (Figure 4b) was found in Fe-STO-600, but the signal at g ~ 2 is assumed to be overlapped by the signal at g = 2.008.

We used extended X-ray absorption fine structure (EXAFS) to analyze the coordination of the Ti and Fe ions in Fe-doped SrTiO₃. Figures 5a–5c show the X-ray absorption spectra recorded for the STO and Fe-STO-600 samples at the Ti K-edge and Fe K-edge. The Fe K-edge X-ray absorption near edge structure (XANES) signals (Figure 5d) with a pre-edge peak at 7113 eV demonstrate that iron is present as Fe³⁺ after annealing in air, which is consistent with the XPS results.[20] The structural parameters derived from the Ti K-edge EXAFS data analyses are summarized in Table 2. The first peak arises from the Ti–O shell with a distance of 1.95 Å, and the second peak originates from the Ti–Sr shell with a distance of 3.35 Å in the Fe-STO-600 sample (Figures 5e and 5f). The Ti–O coordination number in reference SrTiO₃ was found to be 6, confirming perfect coordination.[20] For the Fe-doped SrTiO₃ sample, the coordination number was about 5.6, reflecting the formation of oxygen vacancies in the first shell due to Fe doping in the lattice.[21] The EXAFS fitting results show that the mean Fe–O
bond length is 1.97 Å with a coordination number of 5.1 in the first shell, indicating the presence of Fe$^{3+}$-OV pairs.\(^{[23]}\)

To investigate the possible oxidation mechanism and the function of OVs, \textit{in situ} diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded with Fe-STO-600 and undoped STO in the dark at room temperature. Isopropanol (IPA) was used as a probe molecule to follow the adsorption process (Figures 6a and 6b). When dosing IPA from 0.001 mbar to 0.1 mbar, the typical bands (1128 cm\(^{-1}\) and 1164 cm\(^{-1}\)) assigned to \(\nu_{C-O}\) and \(\nu_{C-C}\) of the isopropoxy species, respectively)

### Figure 5. Absorption spectra (including pre-edge, XANES and EXAFS regions) at Ti K-edge of a) STO and b) Fe-STO-600 samples; c) absorption spectrum at Fe K-edge of Fe-STO sample; d) XANES K-edge spectrum of Fe-STO sample; Fourier Transform and corresponding fits at the e) Ti K-edge and f) Fe K-edge of samples; \(k^3\)-weighted EXAFS oscillations for g) Ti K-edge and h) Fe K-edge of samples.

### Table 2. Curve-fitting results of Ti and Fe K-edge EXAFS in STO and Fe-STO samples.

| Sample | Shell | CN\(^{[a]}\) | R\(^{[b]}\) (Å) | DW\(^{[c]}\) (Å) | \(\Delta E_0\)\(^{[d]}\) | R factor [%] |
|--------|-------|-------------|----------------|----------------|----------------|-------------|
| STO    | Ti-O  | 6.0         | 1.91337        | 0.02069        | −9.86203       | 0.00187     |
|        | Ti-Sr | 8.0         | 3.07223        | 0.00008        | −19.93359      |             |
| Fe-STO | Ti-O  | 5.6         | 1.94555        | 0.01085        | −6.46852       | 0.00467     |
|        | Ti-Sr | 8.0         | 3.35371        | 0.00892        | −10.51012      |             |
| Fe-STO | Fe-O  | 5.1         | 1.97213        | 0.00929        | −5.72723       | 0.01840     |
|        | Fe-Sr | 8.0         | 3.34120        | 0.01908        | 0.78261        |             |

[a] CN: coordination number, [b] R: bond distance, [c] R factor: Debye-Waller factor, [d] \(\Delta E_0\): Inner potential correction.

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA.
from isopropoxy generated by dissociative chemisorption were emerging for both the doped and the undoped sample. According to the Gu et al. and Shkrob et al., chemisorbed IPA can originate from two pathways (Figure 6f): i) condensing with a Ti-OH group forming isopropoxy species and releasing water; ii) binding to undercoordinated Ti sites through the hydroxyl O by dissociative adsorption and releasing a proton (H\(^+\)). It is reasonable to anticipate that the latter approach is more favored than the former one. We then compared the intensity of the band at 1128 cm\(^{-1}\) with that at 2972 cm\(^{-1}\) to explore the percentage of chemisorbed IPA for the Fe-doped and undoped STO samples with respect to the different dosing pressures of IPA as shown in Figures 6c and 6e. When dosing 0.001 mbar of IPA, the intensity ratio of \(\nu(C-O)/\nu(C-H)\) for Fe-STO is 0.54 compared with 0.37 for STO (Figure 6c). With increased dosing of 0.01 mbar, the intensity ratio for Fe-STO is 0.62, while that for STO is 0.47 (Figure 6d). In the case of dosing 0.1 mbar of IPA, the intensity ratios for Fe-STO and STO are 0.92 and 0.83, respectively (Figure 6e). The comparison indicates that the favored chemisorption of IPA on Fe-STO compared with STO is less pronounced when increasing the dosed amount due to the increased condensation of Ti–OH and IPA for higher IPA dosing. Nevertheless, the favored chemisorption of IPA on Fe-STO is clearly detected arising from the defect structure as confirmed by the EXAFS and EPR results.

It has to be noted that for both Fe-STO and STO trace amounts of chemisorbed isopropoxy species can be oxidized to adsorbed acetone as indicated by the band at ca. 1700 cm\(^{-1}\) (Figure 6c), which disappeared in the following DRIFT spectra dosing 0.1 mbar of IPA due to its desorption into the gas phase or further surface reaction. This observation suggests that the chemisorbed isopropoxy species is an important intermediate in the dehydrogenation of IPA.

Conclusions

We demonstrated that the highly selective photocatalytic alcohol conversion to the corresponding carbonyl compounds with simultaneous \(\text{H}_2\) evolution in one reaction system under visible light and anaerobic conditions can be achieved using Fe-doped SrTiO\(_3\) with deposited Pt NPs. The activation of \(\alpha\)-C–H bonds is
bonds in the alcohol molecules by surface oxygen vacancies and the limited oxidation potential of Fe-doped SrTiO$_3$, due to the fine-tuned valence band edge contributed to the high selectivity and good activity. This study not only provides an environment-friendly route to simultaneously produce $\text{H}_2$ and carbonyl compounds, but also supplies a more economical photocatalyst for mild organic conversion via solar energy utilization.

**Acknowledgement**

We sincerely acknowledge the financial support by the Max Planck Society (Max Planck Fellowship, IMPRS RECHARGE), the Alexander von Humboldt Foundation, DFG (SFB/TRR 247), National Key Research and Development Program of China (2017YFA0207002), NSFC (21836001) and Science Challenge Project (TZZ016004).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Anaerobic alcohol conversion • SrTiO$_3$ • Oxygen vacancy • Carbonyl compounds • Photocatalysis

[1] a) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Escriu, A. F. Carley, A. A. Herzog, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, Science, 2006, 317, 362–365; b) S. E. Davis, M. S. Ide, R. J. Davis, Green Chem. 2013, 15, 17–45; c) G. L. Brett, Q. He, C. Hammond, P. J. Miedziak, N. Dimitratos, M. Sankar, A. A. Herzog, M. Conte, J. A. Lopez-Sanchez, C. J. Kiely, D. W. Knight, S. H. Taylor, G. J. Hutchings, Angew. Chem. Int. Ed. Engl. 2011, 50, 10136–10139.

[2] a) A. Tanaka, K. Hashimoto, H. Kominami, J. Am. Chem. Soc. 2012, 134, 14526–14533; b) M. Bellardita, E. I. Garcia-Lopez, G. Marcì, I. Krivtsov, J. R. García, L. Palmisano, J. Catal. 2009, 259, 28–33; c) D. Jiang, X.-Y. Sun, J. Lin, J. Phys. Chem. C 2008, 112, 9753–9758; b) Q. Zhang, Y. Huang, S. Peng, Y. Zhang, Z. Shen, J.-J. Cao, W. Ho, S. C. Lee, D. Y. H. Pu, Appl. Catal. B 2017, 204, 346–357; c) P. Li, C.-B. Liu, G.-L. Wu, Y. Heng, S. Lin, A. Ren, K.-H. Lv, L.-S. Xiao, W.-D. Shi, RSC Adv. 2014, 47615–47624.

[3] a) H. Yu, S. Ouyang, S. Yan, Z. Li, T. Yu, Z. Zou, J. Mater. Chem. A 2011, 21, 11347; b) H. Liu, T. Wang, H. Zhang, G. Liu, P. Li, L. Liu, D. Hao, J. Ren, K. Chang, X. Meng, H. Wang, J. Ye, J. Mater. Chem. A 2016, 4, 1941–1946.

[4] Q. Zhang, Y. Huang, S. Peng, T. Huang, J.-J. Cao, W. Ho, S. Lee, Appl. Catal. B 2018, 239, 1–9.

[5] a) J.-L. Fujisawa, T. Eda, M. Hanaya, Chem. Phys. Lett. 2017, 685, 23–26; b) R. Giesecke, R. Hertwig, T. J. M. Bayer, C. A. Randall, A. Klein, J. Am. Chem. Soc. 2017, 100, 4590–4601.

[6] E. Wierzbicka, X. Zhou, N. Denisov, J. Yoo, D. Fehr, N. Liu, K. Meyer, P. Schmuki, ChemSusChem 2019, 12, 1900–1905.

[7] a) A. I. Frenkel, D. Ehre, V. Lyahovitskaya, L. Kanner, E. Wachtel, I. A. Shkrob, M. C. Sauer Jr., D. Gosztola, J. Phys. Chem. C 2011, 115, 2980–2989.

[8] a) A. M. Hofmeister, G. R. Rossman, J. Phys. Chem. C 2011, 115, 14918–14925; b) H.-C. Hao, L. Zhang, W.-Z. Hao, S.-M. Qiao, X.-C. Liu, ACS Sustainable Chem. Eng. 2019, 7, 10501–10508.

Manuscript received: August 8, 2019
Accepted manuscript online: August 9, 2019
Version of record online: September 20, 2019