Oxygen Vacancies Mediated Complete Visible Light Photocatalytic NO Oxidation over BiOCl

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Abstract: In this study, complete visible light NO oxidation mediated by O_2 is achieved over a defect-engineered BiOCl with selectivity exceeding 99%. Well-designed oxygen vacancies on the prototypical (001) surface of BiOCl favored the formation of geometric-favorable superoxide radicals (•O_2^-) in a side-on bridging mode under ambient condition, which thermodynamically suppressed the terminal end-on •O_2^- associated NO_2 emission in case of higher temperatures, and thus selectively oxidized NO to nitrate.
Keywords: Photocatalysis, NOx, Oxygen Vacancy.

1. Introduction

The complete NO oxidation to nitrate during photocatalytic NO removal re-mains a great challenge, which will avoid risky NO_2 emission and also provide potential metabolic nitrogen for micro-organisms. Unavoidable NO_2 generation in contemporary photocatalytic NO removal systems is normally attributed to the presence of one-oxygen reactive species such as holes (O^-) and hydroxyl radicals (•OH), detrimentally leading to the partial NO oxidation ($NO(g) + O^-/•OH \rightarrow NO_2(g)$). In the light of this fact, tuning the formation of oxygen reactive species in the molecular form to dominantly govern complete NO oxidation, particularly super-oxide radicals ($O_2 + e^- \rightarrow •O_2$; $NO(g) + •O_2 \rightarrow NO_3^-$), has been proposed previously.[1,2] Unfortunately, such a •O_2^-based solu-tion still remains debatable because some scientists found that •O_2 could also cause the partial NO oxidation ($NO(g) \rightarrow NO_2(g)/NO_2(aq)^-$). [3,4] The controversy over this issue intrinsically stems from the poor understanding of mechanistic function schemes of •O_2 for NO oxidation on the surface molecular level, especially the influences of specific geometric structures of •O_2 on the reaction selectivity have never been taken into consideration.

2. Experimental

All the theoretical calculations were performed using the first-principles density of functional theory (DFT) + U calculations with the exchange-correlation energy functional, which were described by generalized gradient approximation with Perdew-Burke-Ernzerhof (PBE) exchange-correlation function.

3. Results and discussion

Regarding that the catalytic roles of •O_2 are strongly depend-ent on their delicate structures, a broader DFT study was then carried out to explore the possible NO oxidation pathways and the intermediate species initiated by surface •O_2 in different geometries. When NO approached the terminal end-on •O_2, it was oxidized to peroxynitrite ($OONO^-$) without any barrier, simultaneously releasing 1.32 eV energy (pathway I). Peroxyni-trite is known to be a powerful and toxic oxidant that causes the direct biotoxicity of NO when NO acts as an intercellular messenger in vivo, and also a transient precursor towards the NO_2 formation on metal or metal oxide surfaces. As expected, breaking of the O-O bond in peroxynitrite led to the release of gaseous NO_2 with a barrier of 0.49 eV (Figure 1a). Rather than forming an intermediate species, NO was directly oxidized to nitrate in a monodentate state with an energy change of -2.80 eV (pathway II), which was far more thermodynamically accessible than pathway I. Abstracting a proton from a neighboring hydroxyl or adsorbed water by nitrate to-wards the formation of HNO_3* was also energy-favorable with an energy release of 1.64 eV. Moreover, energy expenditure towards the diffusion of nitrate or HNO_3 on the surface was only 0.20 eV, much smaller than that (0.49 eV) of NO_2 desorption (Figure 1a). Since geometric transformation from peroxyni-trite to its structural isomer of nitrate was up against a high barrier of 1.03 eV, NO oxidation via pathway I or II was rather independent (Figure 1b). This comparison clearly demonstrated $•O_2^-$ ensured the reliable NO oxidation, which was theoretically a geometric-sensitive process. As soon as O_2 was adsorbed on the OV of BiOCl(001) surface, instant electron back donation from the OV to O_2 occurred as depicted by the localized electrons depletion on two Bi atoms around the OV and electrons accumulation on the coordinating O_2 (Figure 1c). Partial density of states (DOS) of side-on bridging O_2 contained two occupied spin-up majority states and one occupied spin-down minority state below the Fermi energy, as well as an empty spin-down minority states near the conduction band, revealing the filling of one O_2 2π* orbital toward the $•O_2$ formation (Figure 1c). Along with the nitrate formation, side-on bridging $•O_2$ was then found to inter-act rigorously with NO according to a significant charge depletion of N atom and an extraordinary electron gaining by three O atoms, manifesting an outstanding oxidative ability (Figure 1d). Meanwhile, 2π orbitals of $•O_2$ underwent a considerable broad-ening and were shifted below the valence band maximum (VBM) of BiOCl, indicating the complete NO oxidation by side-on bridging $•O_2$ (Figure 1d).

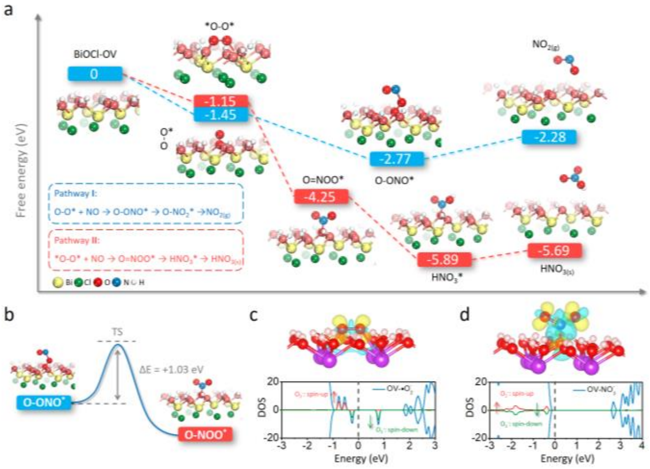

Figure 1. (a) Free energy change against the reaction coordinate for the oxidation of NO by $•O_2$- on BiOCl(001) surface in different geometries. (b) Geometric transition from peroxynitrite to ni-trate. TS represents transition state. Charge density difference and O_2 partial DOS of the (c) O_2-adsorbed and (d) nitrate-adsorbed BiOCl(001) surface.

4. Conclusions

In conclusion, we have utilized a defect-engineered BiOCl to remove NO under visible light, aiming to avoid partial NO oxi-dation and gain mechanistic insight into the intrinsic catalytic roles of $•O_2$-. Well-designed catalytic OVs on the prototypical (001) surface of BiOCl favors the formation of geometric-favorable superoxide radicals ($•O_2$) in a side-on bridging mode under ambient conditions, which thermodynamically sup-pressed the terminal end-on $•O_2$ associated NO_2 emission in case of higher temperatures, and thus selectively oxidized NO to nitrate. These findings will provide the instructive information on exploring the intriguing surface chemistry of photocatalytic NO oxidation and developing highly efficient NOx removal systems.

References

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