

Enhanced carbocatalytic alcohol oxidation by Graphene Acid: Mechanistic insights for the control of the selectivity.

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Graphene oxide (GO), the most prominent carbocatalyst for several oxidation reactions, has severe limitations due to the overstoichiometric amounts required to achieve practical conversions.[1] Graphene Acid (GA), a well-defined graphene derivative fully covered by carboxylic groups but maintaining the electronic conductivity of pristine graphene,[2] sets new activity limits in the oxidation of alcohols working in the catalytic range (5 %wt. vs substrate) with catalytic amounts of HNO₃ acting as co-catalyst. Indeed, GA converts benzyl alcohol to the benzaldehyde overpassing other reported carbo- and metallic catalysts for this general oxidation,[3] with an outstanding activity of 152 mmol converted per gram of catalyst and hour. Benchmark GO, however, did not show catalytic activity in the studied experimental set-up. According to experimental data and first principle calculations, the selective and high-density functionalization with carboxyl groups, combined with electronic conductivity, enhanced the surface oxidation of the co-catalyst HNO₃ and the conversion of the alcohol in the oxidized product. Furthermore, the controlled structure also allows to shed light regarding critical steps of the mechanism, such as the generation of the key organic nitrites intermediates, to regulate precisely the oxidation selectivity towards either possible oxidation products, and the terminating steps of the cycle, where O₂ acts as final oxidant (Figure 1).

References

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Figures

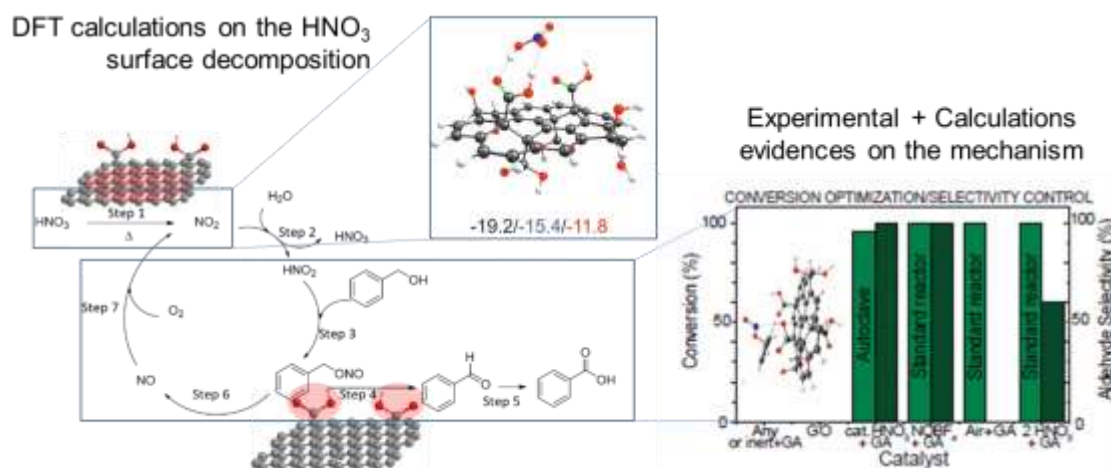


Figure 1: Systematic mechanistic investigation on the HNO₃-mediated alcohol oxidation catalyzed by GA.