CATALYTIC MECHANISMS

Radically active

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Boron nitride (BN) has recently gained the attention of the catalysis community due to its unexpected activity. Despite often being considered inert, important industrial processes including acetylene hydrochlorination and propane dehydrogenation have been successfully conducted using different forms of this nanomaterial as the catalyst. Although such studies have tentatively identified vacancies and defects as being responsible for BN reactivity, a clear mechanistic picture is still missing. Now, Wenrong Yang, Ying Chen and colleagues report evidence to support boron centred radicals as the catalytically active species in boron nitride.

Using ESR spectroscopy the authors assessed the ability of different BN forms — including nanosheets and nanoparticles — to quench 2,2-diphenyl-1-picrylhydrazyl (DPPH), a stable free radical species. DFT calculations suggested the formation of boron radicals at the defects and edges of BN nanosheets. Therefore, exfoliation of the nanosheet structures via sonication was employed to improve the scavenging activity of the compounds studied, by generating further defects and unsaturated boron atoms through the cleavage of boron–nitrogen bonds. Interestingly, nanosheets with different termination

and functional groups — including amino and hydroxyl groups — showed a similar reactivity, supporting the hypothesis that the formed radicals are centred on boron rather than on oxygen or nitrogen atoms. In further experiments, the team applied a boron nitride nanosheet as catalyst for the oxidation of 3,5,3',5'-tetramethylbenzidine (TMB, pictured) in the presence of hydrogen peroxide. Here, BN promotes the catalytic decomposition of H_2O_2 to generate hydroxyl radicals, which in turn react with the colourless TMB resulting in the formation of a blue coloured species — a charge transfer complex of the diimine oxidation product and TMB itself. The formation of OH radicals was verified by ESR spectroscopy using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the trapping agent.

The present study identifies an important mode of reactivity that may impact synthetic schemes based on boron nitride as the catalyst. However, further investigation in this area is required to reconcile previous mechanistic interpretations with the present findings.

Davide Esposito

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