

# The multiface of boron in boron-based propane oxidative dehydrogenation

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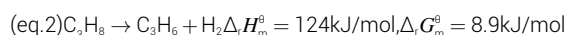
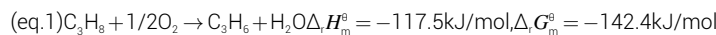
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The boron-based materials have been widely used in heterogenous catalysis including electrocatalysis, thermal catalysis, and photocatalysis. In recent years, boron-based materials have demonstrated remarkable catalytic performance in oxidative dehydrogenation of propane (ODHP), and call for extensive studies to understand the underlying mechanisms governing the high propylene selectivity and low deep oxidation. In this perspective, the state-of-the-art mechanistic understanding of boron-based materials catalyzed ODHP was first presented. The discussion then focused on the "multiface" character of boron under ODH conditions, which refers to its ability to adopt multiple forms, i.e.  $sp$ - ( $-B=O$ ),  $sp^2$ - ( $-BOH$ ,  $>BOB<$ ,  $>BOOH$ ), and  $sp^3$ -hybridization ( $\equiv BOH$ ) modes. This multiface character was analyzed in terms of the structure and reactivity of these boron species, as well as their roles in the C-H activation of propane and the suppression of deep oxidation. This knowledge frames a guideline for the knowledge-driven discovery of key boron species, and implicates to the rational design of boron-based ODH catalysts and radical scavengers.

## INTRODUCTION

Boron is the fifth element in the periodic table with an electronic configuration of  $1s^2 2s^2 2p^1$ , and displays unique medium electronegativity and electron deficiency characteristics. As an element on the border line between metals and nonmetals, it presents chemical properties similar to Si and As, and can adopt in diversified structures and chemical bonds. Boron often utilizes three valence electrons to form two-center two-electron (2c-2e) bond or three-center two-electron (3c-2e) bond in many boron-based materials. Due to the special electronic properties of boron-based materials, they have been used in heterogenous catalysis, especially in the oxidative dehydrogenation of propane (ODHP).

ODHP (eq.1) is considered a promising protocol alternative to the industrialized direct dehydrogenation route benefitted from its low energy input, high atom economy, and free of coking. In contrast to the serious deep oxidation suffered in the metal-based ODH systems, e.g. V, Cr, Co, Mo, the recent discovered nonmetal boron-based catalytic systems exhibit remarkable performance with high propylene selectivity and trace amounts of deep oxidation products., Hermans et al.<sup>1</sup> and Lu et al.<sup>2</sup> reported a propylene selectivity of around or above 80% at a propane conversion of around 20.6%. These novel and fascinating discoveries promote investigations of other boron-based materials, e.g. silicon boride ( $B_6Si$ ), boron carbide ( $B_4C$ ), boron phosphate ( $BPO_4$ ), boron phosphide (BP), and all of them exhibit promising abilities in ODHP.<sup>3</sup>



It is now established that boron is the governing element in the catalysts. The catalysts exhibit similar catalytic reactivity. This is attributed to the similar speciation of oxygenated boron species, which is influenced by the microenvironment. To anchor boron on the supports, Lu et al.<sup>4</sup> reported mesoporous silica-supported boron oxide catalysts which has the great activity in low temperature. At 450°C, the propane conversion of 14.8% can be achieved, with a selectivity of 73.3% toward propylene or 87.4% for both propylene and ethene.

## Mechanisms of boron-based catalysts in ODHP

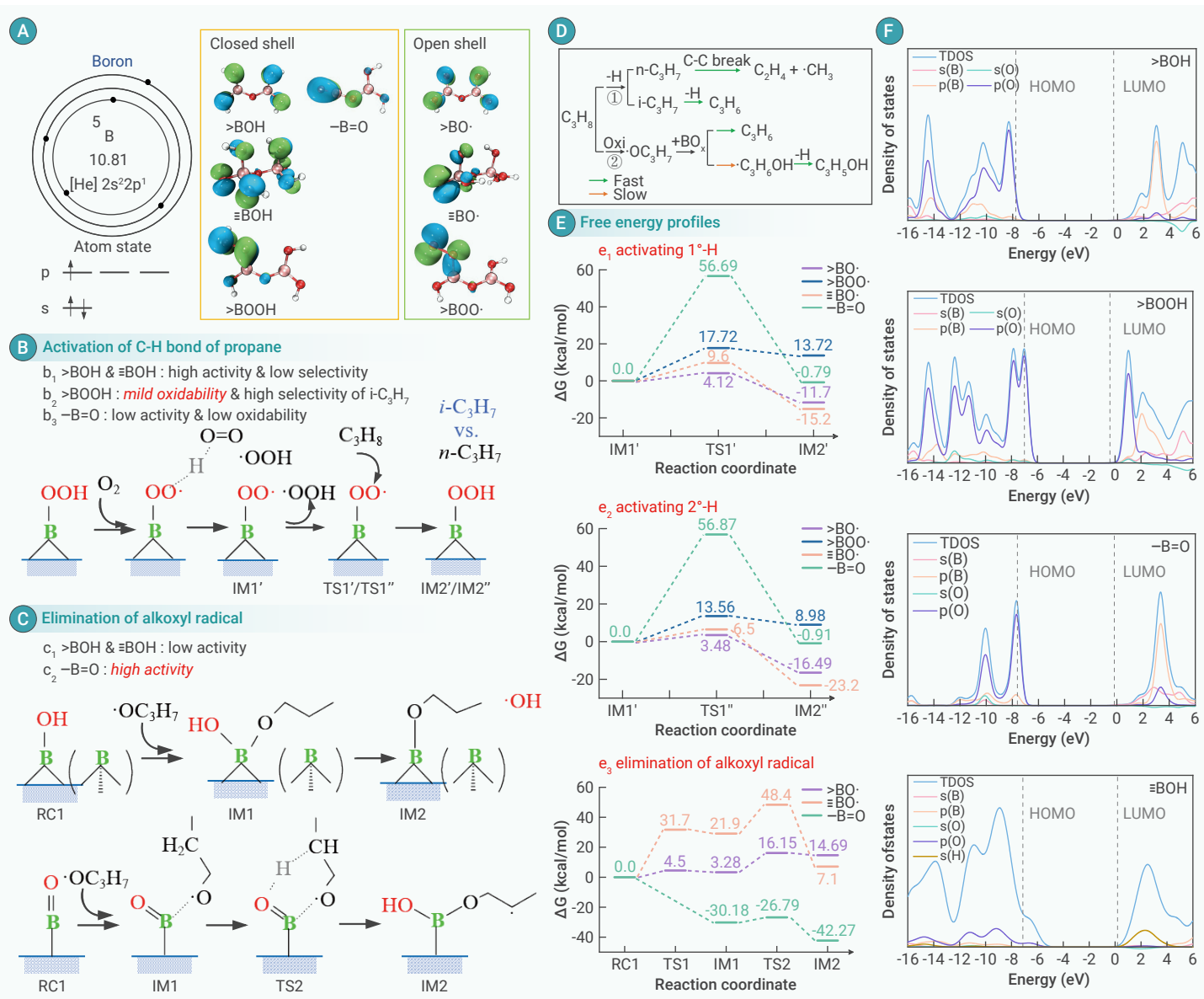
The ODHP catalyzed by boron-containing materials mapped a complicated reaction network featured by cooperated on-surface and off-surface (gaseous) reaction channels.<sup>2,4-9</sup> Different from the Mars-van Krevelen mechanism of metal-based ODH systems that oxidizes propane by lattice O atoms, the boron-based ODHP reactions proceed following a radical-mediated mechanism and make use of gaseous dioxygen directly. Edge oxygenated boron species, denoted as  $>B-OH$  or  $BO_x(OH)_{3-x}$  ( $x \leq 3$ ) have been proposed to be the responsible site for the catalytic ability of boron-containing materials in ODH based on <sup>11</sup>B NMR measurements and DFT calculations (Figure 1A),<sup>2,5,8</sup> and a complex reaction network enveloping three stages has been mapped starting from these species by means of DFT calculations, i.e. the initiation of the reaction by activation of dioxygen at the oxygenated boron sites, the propagation of chain reactions accounting for the oxidative dehydrogenation of propane to olefins and other oxidative products, and finally the termination stage during which the reactive species are eliminated.<sup>9-10</sup>

The reaction is triggered by the activation of dioxygen colliding on the surface, which generates gaseous hydroperoxy species ( $HOO\cdot$ ) and surface dangling bonds ( $>BO\cdot$ ,  $>BOO\cdot$ ,  $\equiv BO\cdot$ ). These nascent active species then convert propane to olefin products via two sequential dehydrogenation steps. The in situ formed water molecules can crack the  $>B-O-B<$  bond to breed more  $>B-OH$  sites. In its high presence, water can peel off surface  $B_xO_y$  clusters which results in boron leakage. This emphasizes the proper control of the humidity in the reaction system, implicating the necessity for delicate optimization of gas flow. Under ODH conditions, the rich presence of oxidative species, e.g. the co-fed dioxygen and the in situ formed  $HOO\cdot$  and  $HO\cdot$  species, make it possible for them to capture propyl radical intermediate and form corresponding oxygenated species. In view of the extremely low deep oxidation of propane in the boron-based ODH systems, the majority of these oxygenated species can be consumed and put back to the right track to form olefin rather than further oxidized to  $CO_x$  or other by-products. According to computational mechanistic studies, the unique ability of boron-containing catalysts to suppress deep oxidation of propane can be attributed to the oxophilicity of boron, either in its native form in the freshly fabricated catalysts ( $>BOH$ ,  $>BOB<$ ,  $>BOOH$ ,  $\equiv BOH$ )<sup>8,9</sup> or in the in situ formed species under ODH conditions ( $>BOOH$ ,  $-B=O$ ).<sup>5-6</sup>

The above-mentioned character of the ODH reactions that embody multiple boron species in the reaction network can be attributed to the ability of boron to facilely transform between its  $sp^2$  and  $sp^3$  hybridization modes, and the low melting points of boron oxides enable the co-presence of these oxygenated boron species via surface reorganization of boron-based catalysts under ODH conditions.

## Multiple faces of boron under ODHP conditions

According to calculations, the tri-coordinated boron species,  $>BOH$  and  $>BOOH$ , can donate their H atoms to dioxygen and form  $>BO\cdot$  and  $>BOO\cdot$  dangling bonds, which then activate the C-H bond of propane (Figures 1B-C IM1'-TS1'/TS1"-IM2'/IM2"). In view of the calculated free energy barriers ( $\Delta G^\ddagger$ ),  $>BO\cdot$  is more reactive on activating C-H bond of propane ( $\Delta G^\ddagger = 3.48$  ( $2^\circ-H$ ) or 4.12 kcal/mol ( $1^\circ-H$ )), and  $>BOO\cdot$  behaves as a mild oxidant ( $\Delta G^\ddagger = 13.56$  ( $2^\circ-H$ ) or 17.72 kcal/mol ( $1^\circ-H$ )).<sup>6,8</sup> These data show that  $>BOO\cdot$  exhibits higher selectivity to activate  $2^\circ-H$  to generate  $i-C_3H_7$  radicals than  $>BO\cdot$ . Since the  $i-C_3H_7$  radical has much higher propensity to further dehydrogenate at its methyl group to form olefin than to break its C-C bond (bond energy: 35.9 vs.



**Figure 1.** The electronic structure analysis of active boron species and free energy profiles of key steps in ODHP (A) The HOMO orbitals of boron species; (B) The reaction pathway of propane dehydrogenation at  $>BOH$ ,  $\equiv BOH$ ,  $>BOOH$  and  $-B=O$  sites (from  $b_1$  to  $c_3$ ); (C) The reaction pathway of eliminate alkoxy radicals at  $>BOH$ ,  $\equiv BOH$  and  $-B=O$  sites (from  $c_1$  to  $c_2$ ); (D) The two pathways which prevent the deep oxidation of propane; (E) The Gibbs free energy profiles (298.15 K, 1 atm) for the  $1^\circ H$  ( $e_1$ ),  $2^\circ H$  ( $e_2$ ) activating of propane at  $>BOH$ ,  $\equiv BOH$  and  $-B=O$  sites and alkoxy radical elimination ( $e_3$ ) at  $>BOH$ ,  $\equiv BOH$  and  $-B=O$  sites; (F) Analysis of density of states (DOS) of  $-B=O$ ,  $>BOH$ ,  $\equiv BOH$  and  $>BOOH$  sites.<sup>5-7</sup>

100.0 kcal/mol for  $1^\circ C-H$  vs.  $2^\circ C-1^\circ C$  in  $i-C_3H_7$  (Figure 1E), while the  $n-C_3H_7$  radical shows opposite preference, higher yield of  $i-C_3H_7$  radical means high olefin selectivity. This suggests that in the early stage of propane activation, boron peroxy species ( $>BOOX$ ,  $X=B, H$ , or dangling bond) can contribute to the unique ability of boron-catalysts to suppress deep oxidation by promoting  $i-C_3H_7$  formation.

The  $sp^3$  hybridized boron species ( $\equiv BOH$ ), e.g. in cubic boron nitride ( $c-BN$ ) and  $BPO_4$ , show much weaker ability to donate its H atom to form  $\equiv BO$  (Figure 1B,  $\Delta G^\ddagger = 57.8$  kcal/mol). The  $\equiv BO\cdot$  can grab the hydrogen atoms from propane with  $\Delta G^\ddagger \sim 10$  kcal/mol (6.5 kcal/mol for  $2^\circ H$  and 9.6 kcal/mol for  $1^\circ H$ ).<sup>7</sup> These values also indicate that tetra-coordinated boron species has lower activity to dehydrogenate propane.

Regarding the unique ability of boron-based catalysts to suppress propane deep oxidation,<sup>6,8,9</sup> besides the above pathway in the early stage of propane activation, it is also necessary to eliminate the alkoxy intermediates formed in the late stage upon the collision of propyl radical with oxidative species, e.g.  $O_2$ ,  $HOO\cdot$ , and  $HO\cdot$ . These alkoxy intermediates are considered to be important intermediate species that lead to deep oxidation products, and

need be consumed in order to block the deep oxidation of propane to  $CO_x$  (Figure 1D).

The affinity of  $>BOH$  and  $\equiv BOH$  for alkoxy radicals were assessed, and this reaction proceeds in a two-step manner: The alkoxy radical first binds to B site via its O atom, then the B atom releases one of its native oxygenated group, e.g.  $\cdot OH$  radical, to maintain its favorable hybridization mode ( $\Delta G^\ddagger = 16.15$  ( $>BOH$ ) vs. 48.4 ( $\equiv BOH$ ) kcal/mol, Figures 1c1 & e3).<sup>7,8</sup>

In recent study, we reported the in-situ formation of  $sp$ -hybridized transient  $-B=O$  species and its ability as a hunter for alkoxy radicals. The electronic structure analysis indicates that B atom of  $-B=O$  site has strong oxophilicity, and the adsorption of alkoxy radical at the  $-B=O$  group is an exergonic process ( $\Delta G = -30.18$  kcal/mol),<sup>5</sup> which results in a tri-coordinated B species (Figure 1c2, IM1) which accommodates the unpaired electron on the alkyl group via an intro-molecular  $\beta-H$  atom transfer from C to  $-B=O$  group (Figure 1c2, IM1 $\rightarrow$ TS2 $\rightarrow$ IM2). This intermediate can then release propylene assisted by  $\cdot OOH$  radical, and the whole process is exergonic by 26.79 kcal/mol.<sup>5</sup> Note that the  $-B=O$  site is inert in activating C-H bond of propane directly in view of the calculated free energy barriers to the dehydro-

generation ( $1^\circ\text{-H}$ : 56.69 kcal/mol;  $2^\circ\text{-H}$ : 56.87 kcal/mol) (Figure 1E). This can be attributed to the electron-withdrawing nature of the  $\text{-B=O}$  bond that is inert to activate the C-H bond of propane.

The different behaviors of these species are dictated by their bonding nature. According to the analysis of total and partial density of states (TDOS and PDOS) of  $\text{>BOH}$ ,  $\equiv\text{BOH}$ ,  $\text{>BOOH}$  and  $\text{-B=O}$  sites (Figure 1F, the 2p-orbitals of B atom at  $\text{-B=O}$  and  $\text{>BOH}$  sites constitute predominantly the low-energy unoccupied molecular orbitals, while for  $\text{>BOOH}$ , both 2p-orbitals of B and O atoms contribute to the unoccupied orbitals.<sup>9</sup> For  $\equiv\text{BOH}$ , H 1s-orbitals contributes to the unoccupied orbitals.<sup>9</sup> The high-energy occupied orbitals of all boron sites are mainly attribute to O-2p orbitals, which illustrated that O atoms are the nucleophilic sites in the activation of C-H bond.

The NPA charge analysis shows that B atom always carries positive charge with marginal difference ( $\text{-B=O}$ : 1.23,  $\text{>BO}$ : 1.20,  $\text{>BOO}$ : 1.29,  $\equiv\text{BO}$ : 1.31), reflecting the influence of its chemical environment on its electrophilicity.<sup>8,9</sup> Conceptual Density Functional Theory (CDFT) analysis showed that B atom of  $\text{-B=O}$  active sites preferred to occur electrophilic reaction (value of  $f^-$  in  $\text{-B=O}$ ,  $\text{>BO}$ ,  $\text{>BOO}$  are 0.082, 0.029, 0.019).<sup>8</sup> The electrophilicity of O atom in  $\text{-B=O}$  was weaker than that in  $\text{>BO}$  and  $\text{>BOO}$ , which were more oxidative ( $f^-$  values of  $\text{-B=O}$ ,  $\text{>BO}$ ,  $\text{>BOO}$  are 0.005, 0.095, 0.384).<sup>8</sup> The analysis of electronic structure is in accordance with the thermodynamic analysis, and explains the difference in the reactivity of the multiple boron species under ODH conditions.

## CONCLUSION AND OUTLOOK

In this perspective, we presented the state-of-the-art understanding on the mechanisms of boron-based ODHP reactions. The acquired knowledge placed foundation to understand the complex reaction network of ODHP reaction catalyzed by boron-containing materials. This understanding is expected to remain valid for the ODH of other alkanes, and implicate to rational design of boron-based ODH catalysts and radical scavengers in experiments. The key issues are:

(1) tri-coordinated boron is superior over its tetra-coordinated analogue in activating C-H bonds of propane. The  $\text{>BOO}$  active site can work as mild oxidant to selectively dehydrogenate propane at the  $2^\circ\text{-C}$  site, and contributes to the high propylene selectivity by promoting the formation of  $i\text{-C}_3\text{H}_7$ .

(2) the B atom of  $\text{-B=O}$  site has stronger electrophilicity than that of other boron species, and can facily capture alkoxy radicals accessible in its vicinity to block the deep oxidation of propane. This process is both thermodynamic and kinetic favorable.

(3) water promotes the generation of hydroxylated boron species, e.g.  $\text{>BOH}$ , via hydrolysis of  $\text{>B-O-B<}$  bridge. However, large amount of water leads to the loss of boron species and impairs catalysis.

There remain challenges owing to the dynamic surface reorganization of boron-based catalysts under ODH conditions which is hard to study with in situ experimental techniques. The reliable theoretical studies are expected to be involved more actively to co-operate with experimental studies to extend our understanding of the boron catalytic ODHP catalytic system. The investi-

gations should include, but not limited to, identification of key meta-stable species governing the evolution of reaction network, the influence of the microenvironment on the speciation of boron, and the influence of dynamical surface reorganization on the activation of dioxigen and propane.

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## AUTHOR CONTRIBUTIONS

All authors contributed to the manuscript and approved the final version.

## DECLARATION OF INTERESTS

The authors declare no competing interests.