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## Viewpoint

# A viewpoint on catalytic origin of boron nitride in oxidative dehydrogenation of light alkanes

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## ABSTRACT

Oxidative dehydrogenation of light alkanes to alkenes is an attractive alternative route for industrial direct dehydrogenation because of favorable thermodynamic and kinetic characteristics, but encounters difficulties in selectivity control for alkenes because of over-oxidation reactions that produce a substantial amount of undesired carbon oxides. Recent progress has revealed that boron nitride is a highly promising catalyst in the oxidative dehydrogenation of light alkanes because of its superior selectivity for and high productivity of light alkenes, negligible formation of CO<sub>2</sub>, and remarkable catalyst stability. From this viewpoint, recent works on boron nitride in the oxidative dehydrogenations of ethane, propane, butane, and ethylbenzene are reviewed, and the emphasis of this viewpoint is placed on discussing the catalytic origin of boron nitride in oxidative dehydrogenation reactions. After analyzing recent progress in the use of boron nitride for oxidative dehydrogenation reactions and finding much new evidence, we conclude that pure boron nitride is catalytically inert, and an activation period is required under the reaction conditions; this process is accompanied by an oxygen functionalization at the edge of boron nitride; the B-O species themselves have no catalytic activity in C-H cleavage, and the B-OH groups, with the assistance of molecular oxygen, play the key role in triggering the oxidative dehydrogenation of propane; the dissociative adsorption of molecular oxygen is involved in the reaction process; and a straightforward strategy for preparing an active boron nitride catalyst with hydroxyl groups at the edges can efficiently enhance the catalytic efficacy. A new redox reaction cycle based on the B-OH sites is also proposed. Furthermore, as this is a novel catalytic system, there is an urgent need to develop new methods to optimize the catalytic performances, clarify the catalytic function of boron species in the alkane ODH reactions, and disclose the reaction mechanism under realistic reaction conditions.

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## 1. Introduction

Light olefins (C<sub>2</sub>=–C<sub>4</sub>=) are the most important feedstocks in the chemical industry, with a global production of > 200 million metric tons per year, and are currently produced through ei-

ther the cracking of petroleum-derived hydrocarbons or a multistage coal-based methanol-to-olefins process that commonly involves extensive energy consumption and results in enormous carbon emissions [1–3].

The recent increase in the availability of worldwide shale

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gas and natural gas resources, which contain considerable amounts of light alkanes ( $C_2$ – $C_4$ ), has stimulated a quick technical shift to obtaining commodity light olefins through gas-based dehydrogenation routes [4,5]. Taking propylene production as an example, catalytic dehydrogenation of propane (PDH) has supplied ~5% of global propylene, and this is anticipated to increase to 20% by 2020 [6]. Nevertheless, direct dehydrogenation protocols relying on platinum- or chromium oxide-based catalysts practically suffer from thermodynamic limitations in further enhancing the reaction efficiency and also rapid catalyst deactivation through coking and catalyst sintering, and thus require frequent regeneration of the catalysts under harsh conditions [7,8].

Oxidative dehydrogenation (ODH) is an attractive alternative to direct dehydrogenation processes because of favorable thermodynamic and kinetic characteristics, e.g., exothermic, lower reaction temperature, faster reaction rate, and especially no coking [9–11]. In the past few decades, catalytic systems giving good performances in the ODH reaction of light alkanes have been those based on transition metal oxides (e.g.,  $V_2O_5$ ,  $MoO_3$ , and  $NiO$ ) or alkaline-earth metal oxychlorides [12]. However, the formed electron-rich olefins easily react with the surfaces of metal oxide catalysts, resulting in the cleavage of the C–C bond through a subsequent oxygen insertion, thus forming the undesired over-oxidation product,  $CO_2$ . As summarized in Fig. 1(A) for the well-developed metal oxide catalysts, the over-oxidation product,  $CO_2$ , constitutes a very high proportion of the products, typically around 20% and in some cases even 50%, at conversion levels of ~20%, a typical value of industrial interest [13–22]. There is therefore an urgent need to develop new catalysts that can produce olefins with high selectivity under the severe conditions of alkane activation, but this is a great challenge.

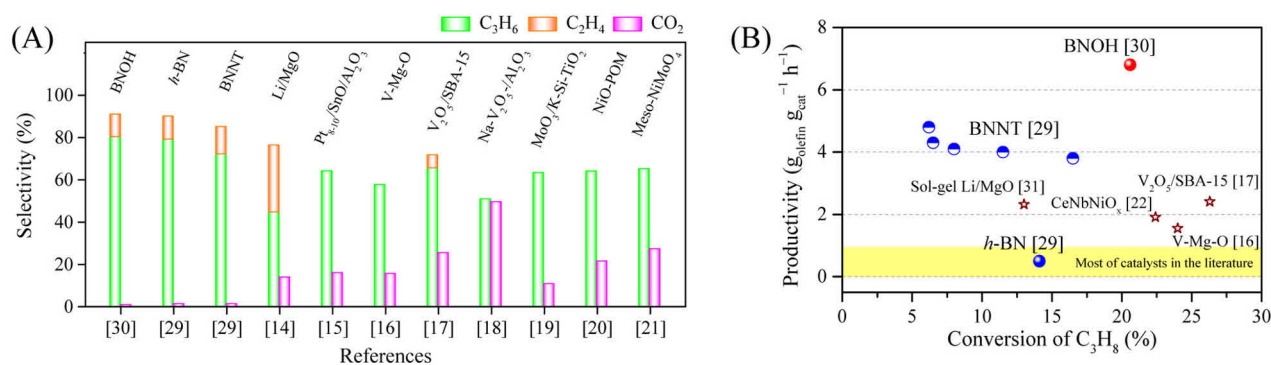
## 2. Boron nitride, an active catalyst for ODH reactions

Boron nitride has been extensively applied in the fields of physics, electronics, and aerospace as a sealing material, taking advantage of its excellent anti-oxidation properties and structural stability [23,24]. In catalysis research, boron nitride is generally considered to be chemically inert, and has been used

merely as a carrier for a long time [25,26]. Also, Fu and Bao [27,28] have confirmed that a boron nitride cover can be used as a promoter to tune molecule-metal interactions and enhance metal-catalyzed reactions. Recently, the Hermans group at University of Wisconsin-Madison, USA, and our research group at Dalian University of Technology, China, independently disclosed that boron nitride could efficiently catalyze the oxidative dehydrogenation of propane to propylene with impressive selectivity, and with only negligible  $CO_2$  formation (Fig. 1(A)) [29,30]. It is important to highlight that such a novel catalyst system addresses the difficulty of selectivity control for olefins that has long existed in oxidative dehydrogenation because of the over-oxidation reactions that produce a substantial amount of undesired  $CO_2$ .

In Hermans' study, hexagonal boron nitride (*h*-BN) exhibited high selectivity for propylene (79%) and ethylene (12%) at a 14% conversion level of propane [29]. In our case, edge-hydroxylation treatment granted boron nitride higher activity (20.6%), selectivity (80.2%), and stability for at least 300 h [30]. Our control experiment with a feed gas of propylene and molecular oxygen also showed that the boron nitride catalyst has almost no activity for propylene oxidation, and thus prevents its over-oxidation to  $CO_2$  [30]. One of the most important requirements for commercially attractive oxidative dehydrogenation catalysts is high productivity ( $g_{olefin} g_{cat}^{-1} h^{-1}$ ) of the olefins. Hexagonal boron nitride exhibited a productivity of ~1  $g_{olefin} g_{cat}^{-1} h^{-1}$  [29], while hydroxylated boron nitride (BNOH) showed a higher olefin production of 6.8  $g_{olefin} g_{cat}^{-1} h^{-1}$  (Fig. 1(B)), which is far higher than those of metal oxide catalysts.

In addition to the ODH reaction of propane, follow-up reports showed that boron nitrides were active catalysts for the oxidative dehydrogenations of *n*-butane and isobutane [32] and ethane [33], with the latter conducted at higher temperatures. The study on ethane ODH also demonstrated the outstanding high-temperature oxidation resistance of boron nitride. For example, using a hydroxylated boron nitride catalyst, at a very high conversion level of 63%, the ethylene selectivity was 80%, which is comparable to that of the industrial steam-cracking route [33]. All of these results confirmed that boron nitride offers rather high selectivity, and only small amounts of  $CO_2$  are



**Fig. 1.** (A) Comparison of selectivities toward light olefins and  $CO_2$  in propane ODH at ~20% conversion for several representative catalysts; (B) Comparison of productivities for olefins of several boron-nitride-based catalysts with those of reported catalysts. Data from Refs. [14–31].

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