



Review Paper

A mini review on oxidative dehydrogenation of propane over boron nitride catalysts



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ABSTRACT

Oxidative dehydrogenation of propane is an attractive route for the synthesis of propylene due to its favorable thermodynamic and kinetic characteristics, however, it is challenging to realize high selectivity towards propylene. Recently, it has been discovered that boron nitride (BN) is a promising catalyst that affords superior selectivity towards propylene in oxidative dehydrogenation of propane. Summarizing the progress and unravelling the reaction mechanism of BN in oxidative dehydrogenation of propane are of great significance for the rational design of efficient catalysts in the future. Herein, in this review, the underlying reaction mechanisms of oxidative dehydrogenation of propane over BN are extracted; the developed BN catalysts are classified into pristine BN, functionalized BN, supported BN and others, and the applications of each category of BN catalysts in oxidative dehydrogenation of propane are summarized; the challenges and opportunities on oxidative dehydrogenation of propane over BN are pointed out, aiming to inspire more studies and advance this research field.

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1. Introduction

Propylene is one of the most important basic industrial chemicals, which could be used as a platform for the production of a variety of organic chemicals, such as acrylonitrile, epichlorohydrin, propylene oxide, isopropanol, acetone, acrylate and etc. (Kumar et al., 2021; Atanga et al., 2018; Węgrzyniak et al., 2015; Cavani et al., 2007). The traditional propylene production process suffers from both low yield of propylene and high consumption of energy. With the outbreak of the shale gas revolution, the synthesis of propylene from propane (separated and extracted from the shale gas) is of great practical significance (Middleton et al., 2017; Bruijninx and Weckhuysen, 2013; Dong et al., 2012; Zhao et al., 2015). In this context, dehydrogenation of propane to propylene emerges worldwide as a more efficient production route

(Belgamwar et al., 2020; Biloen et al., 1977; Mazzocchia et al., 1991; Song et al., 2021).

There are two route to synthesize propylene from propane, direct dehydrogenation of propane and oxidative dehydrogenation of propane, respectively. The direct dehydrogenation of propane that has been industrialized is a strong endothermic reaction, which requires a large amount of energy input. On the contrary, oxidative dehydrogenation of propane is an exothermic reaction, which could be realized at relatively low temperatures. Therefore, it is necessary to develop oxidative dehydrogenation route.

Oxidative dehydrogenation of propane is an effective process for the synthesis of propylene (Wang et al., 2011; Huš et al., 2020; Korzyński and Dincă, 2017). It is promising because of its significant thermodynamic advantages and low energy consumption requirements. It is an exothermic reaction. Low temperature is conducive to the reaction and less energy is required (Wang et al., 2021). The thermodynamic equilibrium conversion of propane in oxidative dehydrogenation of propane is higher compared with that of non-oxidative propane dehydrogenation at low temperature, and the direct cracking of propane is inhibited to a certain extent, which slows down the rate of catalyst deactivation due to carbon deposition (Kondratenko et al., 2001; Laha et al., 2014; Dury

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et al., 2004; Shangguan et al., 2002). Owing to the advantages of oxidative dehydrogenation of propane, it has become one of the frontier research fields for the comprehensive utilization of low-carbon alkanes.

In order to achieve high activity and high selectivity towards propylene, a number of catalysts have been developed for oxidative dehydrogenation of propane, including vanadium-based catalysts (Liu et al., 2004; Chaar et al., 1988; Eon et al., 1994; Valenzuela and Corberán, 2000; Zhang and Liu, 2018), molybdenum-based catalysts (Abello et al., 2001; Chen et al., 2000; Watson and Ozkan, 2000; Ueda et al., 1998) and rare earth metal catalysts (Fang et al., 1998, 1999; Au and Zhang, 1997; Zhang et al., 1994). Among them, molybdenum-based and vanadium-based catalysts are most widely studied (Fu et al., 2019; Liu et al., 2016). Nevertheless, over these catalysts, the selectivity towards propylene is too low even at a moderate propane conversion rate. In 2016, Grant et al. (2016) revealed that boron nitride (BN) is a promising catalyst that afforded superior selectivity towards propylene in oxidative dehydrogenation of propane. As an example, at 490 °C, 0.15 atm O₂ and 0.3 atm C₃H₈, propane conversion was 14.0% while the selectivity towards propylene and ethylene reached 79.0% and 12.0% respectively. Compared with these metal-based catalysts, BN catalysts greatly improve the selectivity for propylene and ethylene. Moreover, the application of BN catalyst in propane oxidative dehydrogenation could reduce the reaction cost and energy loss. The unique and hitherto unanticipated performance of BN initiated the researches of oxidative dehydrogenation of alkanes over BN-based catalysts (Tian et al., 2019; Shi et al., 2018a, b; Garro-Mena et al., 2019; Loiland et al., 2019; Li et al., 2019; Qian et al., 2013).

Up to now, a series of BN-based catalysts have been applied for oxidative dehydrogenation of propane, including pristine BN (Chaturbedy et al., 2018; Yusuke et al., 2018), functionalized BN (Shi et al., 2017a, b; Li et al., 2022), supported BN (Wang et al., 2020; Belgamwar et al., 2020; Dong et al., 2020) and several others (Wu and Lin, 2008; Zhang et al., 2022) (Scheme 1). In this review, we summarize the progress of each category of above-mentioned BN-

based catalysts in oxidative dehydrogenation of propane, extract the underlying reaction mechanisms, and point out the challenges and opportunities, with the target to inspire more studies and advance this research field.

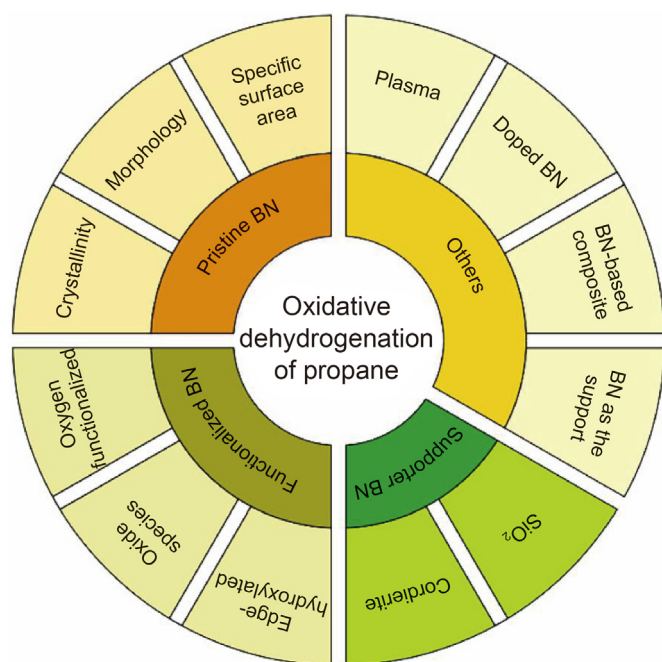
2. Mechanism of oxidative dehydrogenation of propane over BN-based catalysts

Since the discovery of the superior performance of BN in oxidative dehydrogenation of propane in 2016 by Grant et al. (2016) numerous investigations have been carried out to unravel the underlying reaction mechanisms, with the aim to understand the reaction path from a molecular/atomic level and lay a theoretical foundation for the design of highly efficient catalysts (Shi et al., 2018a, b; Li et al., 2020; Zhang et al., 2018). According to the proposed active sites and reaction pathways, the mechanisms could be roughly divided into seven categories (Love et al., 2019a; Lu et al., 2019).

- ① B(OH)_xO_{3-x} as the active site. Love et al. (2019b) discovered that there was a substantial increase of surface oxygen content in BN after its exposure to oxidative dehydrogenation of propane reaction atmosphere. In order to make clear the oxygenated surface species, the authors investigated the structural transformation of BN catalysts before and after the oxidative dehydrogenation of propane reaction by ¹H–¹¹B nuclear magnetic resonance, scanning electron microscopy and X-ray absorption spectroscopy, and revealed that BN was readily oxidized and hydrolyzed under the oxidative dehydrogenation of propane reaction, yielding a three coordinated boron site (B(OH)_xO_{3-x}) with variable number of hydroxyl groups and bridging oxidation groups. B(OH)_xO_{3-x} was determined as the active center (Love et al., 2019a).
- ② BO_x as the active site. Initially, oxygen terminated armchair edge of BN (>B–O–O–B<) is considered as the active site (Grant et al., 2016). By combining the catalytic activity of BN in oxidative dehydrogenation of propane with spectroscopic data, kinetic analysis and density functional theory (DFT) calculation, Grant et al. (2016) speculated that >B–O–O–B< abstracted a hydrogen atom from the secondary carbon of propane and broke the O–O bond to form B–OH group and nitroxyl radical, accompanying the generation of propyl radical. Then a second hydrogen atom was abstracted from the primary carbon of propane and created a dipropoxyl intermediate, which gave propylene after desorption and regenerated the >B–O–O–B< active site after oxygen addition (Fig. 1(a)) (Grant et al., 2016).

In addition to BN, Grant et al. (2017) discovered that a series of boron containing compounds, including elemental B, B₄C, TiB, NiB, CoB, HfB₂ and WB, also gave exceptionally high selectivity towards propylene and ethene in oxidative dehydrogenation of propane. X-ray photoelectron spectroscopy analysis revealed that these boron containing compounds exhibited similar surface element composition under oxidative dehydrogenation of propane reaction, primarily B and O atoms. The difference in binding energies of B before and after reaction confirmed that B was oxidized in oxidative dehydrogenation of propane, yielding BO_x sites. It is speculated that BO_x sites may be the active center (Grant et al., 2017).

Through X-ray photoelectron spectroscopy analysis and *in situ* X-ray diffraction characterization, Lu et al. (2019) discovered that the surface BO_x species were gradually formed and stabilized in the reaction atmosphere of oxidative dehydrogenation of propane, showing a consistent trend with the catalyst activity and confirming the viewpoint that BO_x species proposed by Grant et al. (2017)



Scheme 1. Schematic illustration of BN catalysts for oxidative dehydrogenation of propane.

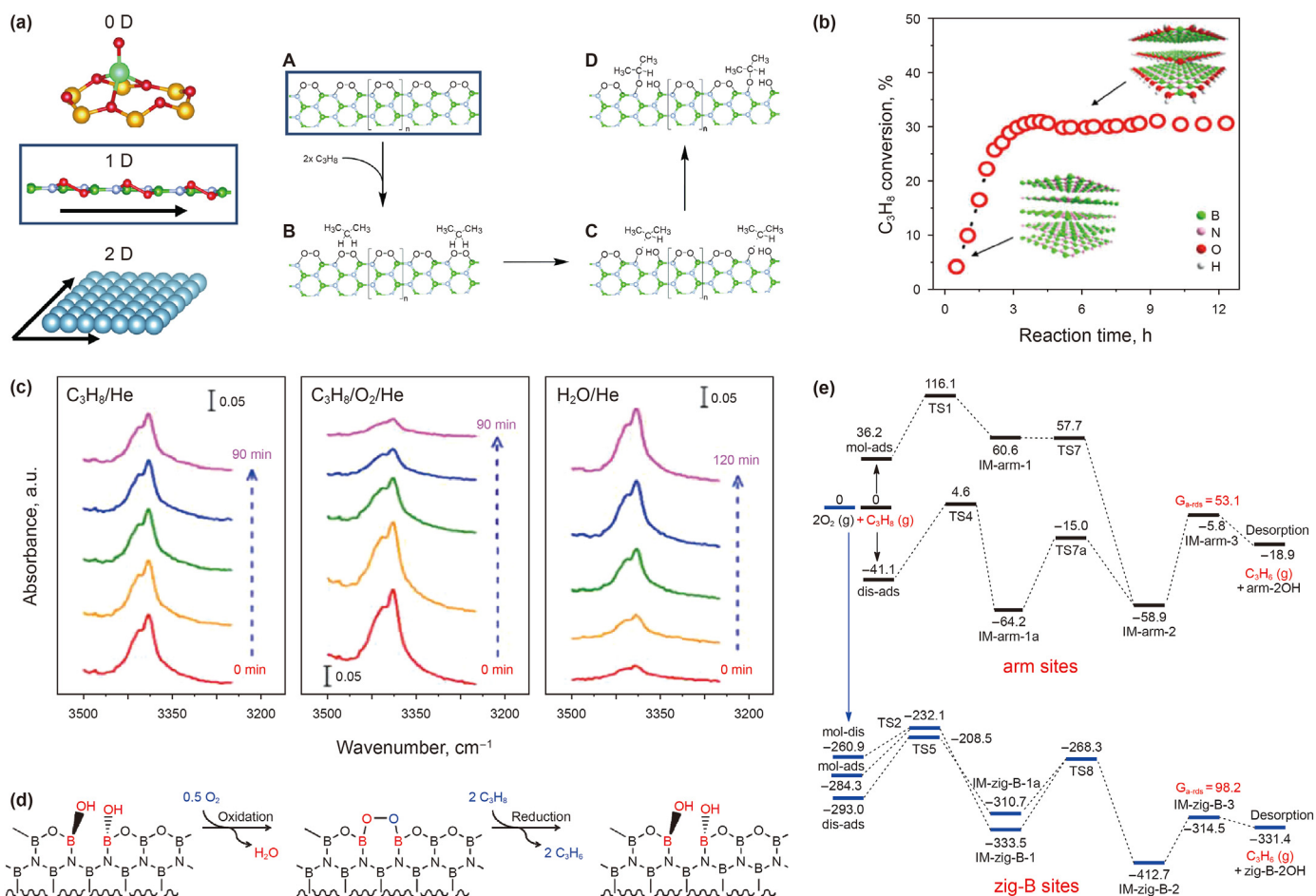


Fig. 1. (a) Schematic illustration of the reaction mechanism for oxidative dehydrogenation of propane over BN proposed by Grant et al. (2016). (b) Catalytic performance of BN in oxidative dehydrogenation of propane. (c) *In situ* infrared spectroscopy study of BN under different reaction atmosphere. (d) Proposed reaction pathway of oxidative dehydrogenation of propane over BN where B–OH as the active sites. (e) Free energy profiles of oxidative dehydrogenation of propane over armchair and zig-B sites. Reproduced with permission from references (Grant et al., 2016), (Li et al., 2019), (Shi et al., 2017a, b) and (Shi et al., 2018a, b).

may be the active center (Shi et al., 2018a, b). When BN was used as catalyst for oxidative dehydrogenation of propane, it underwent an activity induction period before exhibiting excellent propane conversion and selectivity towards propylene (Fig. 1(b)) (Shi et al., 2018a, b).

Kumar et al. (2022) put forward the hypothesis that among these BO_x species, >B–O–O–B< and >B–O–B< were essential for the oxidative dehydrogenation of light alkanes. The O atoms in >B–O–O–B< and >B–O–B< were of different nature, with the O atoms in >B–O–O–B< gaining significant charges while O atoms in >B–O–B< losing charges. The nature of the O atoms in the two species and the Bader charges of C and H in propane guided the H transfers, where >B–O–O–B< and >B–O–B< were responsible for the first and second H transfer, respectively.

③ B–OH group. Using K-edge electron energy loss spectroscopy, X-ray photoelectron spectroscopy, two-dimensional multiple-quantum magic angle spinning nuclear magnetic resonance and infrared spectroscopy, Shi et al. (2017a, b) confirmed the coexistence of zig-zag boron terminated edges, B–O–B and B–OH groups at the edges of active BN. Under the case that only propane was pulsed into BN catalyst, no propane conversion was detected; on the contrary, if propane and oxygen were co-fed into BN, the intensity of B–OH groups detected by *in situ* infrared spectroscopy decreased, accompanying with the

generation of propylene (Fig. 1(c)) (Shi et al., 2017a, b). Taking the kinetic analysis that the reaction order of propane was two into consideration, Shi et al. proposed a reaction pathway and believed that B–OH group was the active center (Fig. 1(d)) (Shi et al., 2018a, b).

- ④ Boron atoms at the defective sites as the active center. This hypothesis was raised up by Creaser et al. (1999), who conducted DFT calculations to unravel the origin of activity of BN in oxidative dehydrogenation of propane, in which reactant adsorption, propylene formation and active site regeneration were taken into consideration. From activity survey, boron zigzag edge, boron atoms neighbor to the nitrogen defective sites and B=O at zigzag edges were proved promising than others, in which boron atoms neighbor to the nitrogen defective sites accounted for the intrinsic reactivity. The boron atoms at the defective sites bonded to carbon in propane strongly, which dissociated the C–H bonds in propane. After the abstraction of two H atoms in propane, propylene was formed and the active sites were hydroxylated into B–H and O–H. Then the oxygen molecules oxidized B–H to B–OH and two adjacent B–OH groups dehydrated to form H₂O and regenerate the active sites (Cao et al., 2020).
- ⑤ Boron-atom-terminated zigzag (zig-B) as the active site. Li and co-authors investigated the mechanism of oxidative dehydrogenation of propane over BN using DFT calculations, focusing on

pathways of O₂ activation and oxidative dehydrogenation of propane (Li et al., 2019). They selected armchair site, zig-B and nitride-atom-terminated zigzag (zig-N) as the hypothetical active sites. It revealed that O₂ followed a dissociated adsorption pathway, and zig-B was the most active site from the kinetic and thermodynamic point of view. The free energy profiles in Fig. 1(e) suggested that the energy level of oxidative dehydrogenation of propane on the zig-B site required the lowest activation energy, indicating zig-B was the potential active site (Li et al., 2019).

- ⑥ N₂O or NO_x-type active site. Rajbanshi and co-authors combined DFT and microkinetic modeling to explore the active sites on oxygen adsorbed BN in oxidative dehydrogenation reaction, adopting the most stable oxygen adsorbed edge for the mechanistic study (Rajbanshi et al., 2020). Calculations predicted that the oxygen adsorbed five membered modified zigzag N-edge, with a N₂O or NO_x-type site, was highly active and selective for oxidative dehydrogenation of propane. N₂O or NO_x-type active site catalyzed oxidative dehydrogenation of propane via two pathways. (1) In heterogeneous catalysis, it followed a redox pathway. C₃H₈ reacted with the catalyst forming C₃H₆ and H₂O, leaving oxygen vacancies on BN; then the oxygen vacancies were replenished by gaseous O₂, completing a catalytic cycle. (2) N₂O or NO_x-type active site could generate gas phase C₃H₇·, which consequently trigger the gas phase reactions (Rajbanshi et al., 2020).
- ⑦ Radical mechanism. In oxidative dehydrogenation of propane, in addition to the desired product propylene, several byproducts such as ethane, ethene and methane (short for C₁ and C₂ byproducts) were also generated. In order to explain the generation of these byproducts, Tian et al. (2019) proposed that CH₃· might be generated on the surface of BN via C–C bond cleavage, leading to secondary reactions for the generation of the byproducts. Venegas et al. (2020) speculated that oxidative dehydrogenation of propane over BN underwent a reaction mechanism that was composed of surface-mediated formation of radicals over metastable sites and their sequential propagation in the gas phase. Zhang et al. (2020) used online synchrotron vacuum ultraviolet photoionization mass spectroscopy to detect the gas phase and provided the direct experimental evidence for the existence of CH₃·. From this experimental result and DFT calculations, the authors speculated that propylene was generated on the surface of BN via the activation of C–H bond in propane while C₁ and C₂ byproducts were formed via both the surface-mediated and gas-phase radical pathway (Zhang et al., 2020).

3. Oxidative dehydrogenation of propane over BN-based catalysts

Although there are still disputes about the active center of BN in oxidative dehydrogenation of propane, researchers agreed that the surface of BN is gradually oxidized and hydroxylated under the reaction atmosphere (Zhi et al., 2009; Li et al., 2013). The functional groups composed of B and its neighbor O, OH or defective sites are generally regarded as the active center for the surface mediated reaction pathway (Li et al., 2019; Venegas et al., 2018). Based on these reaction mechanisms, up to now, a great number of researches have been conducted to develop BN-based catalysts with better performance in oxidative dehydrogenation of propane (Zhao, 1996).

3.1. Oxidative dehydrogenation of propane over pristine BN

In terms of pristine BN, it has been reported that the specific surface area, morphology, crystallinity, as well as the parameters of the reactor used for performance evaluation play important roles in determining its performance in oxidative dehydrogenation of propane (Bhattacharya et al., 2015; Los et al., 2017; Thomas et al., 2015).

- ① Specific surface area of BN. Generally speaking, the larger specific surface area, the more active sites exposed and consequently the higher catalytic activity. From this point of view, BN with larger specific surface area favors propane conversion. Chaturbedy et al.'s study confirmed this speculation (Chaturbedy et al., 2018). They prepared a BN catalyst with high specific surface area to increase the exposure probability of B and the number of BO_x active centers generated in the reaction atmosphere. At the reaction temperature of 525 °C, the as-prepared BN catalyst gave high propane conversion (~50.0%) and high olefin selectivity (the total selectivity towards propylene and ethene was ~70.0%). Moreover, the catalyst afforded stable performance for 100 h by co-feeding with ammonia (Fig. 2(a)), with its structure nearly unchanged (Fig. 2(b)) (Chaturbedy et al., 2018).
- ② Morphology of BN. Grant et al. (2016) compared the catalytic performance of BN nanotubes (BNNT) and hexagonal BN (h-BN) in oxidative dehydrogenation of propane. They disclosed that BNNT and h-BN exhibited similar product distribution, while BNNT gave a propane conversion rate of ~11% under the conditions of 490 °C, 0.15 atm O₂ and 0.3 atm C₃H₈, one order of magnitude higher than that of h-BN (~1%). Characterization results suggested that, the specific surface area of BNNT was twice larger than h-BN, indicating that there were other factors influencing the activity of BN besides the specific surface area. Spectroscopic analysis and DFT study revealed that there were more exposed >B–O–B< sites on BNNT, which served as the active sites for oxidative dehydrogenation of propane. Both the larger specific surface area and the more exposed active sites contributed to the higher activity of BNNT (Grant et al., 2016). Cao et al. (2020) synthesized a spherical superstructure BN from a boron-containing metal organic framework via a simple solvothermal transformation process. It demonstrated that compared with the commercial BNNT, the as-synthesized BN were rich in oxygen-containing boron active sites, which led to a propane conversion of 58.0%, a propylene yield of 27.8% and an ethene yield of 12.4% at 510 °C (Cao et al., 2020). Wang et al. (2021) synthesized a three-dimensional porous fiber-like BN using the self-assembly of boric acid and melamine. The prepared BN catalyst gave a propylene selectivity of 76.4% (the total selectivity towards alkenes of > 90%) at a propane conversion of 16.4%. Moreover, the BN catalyst remained stable for 200 h at 520 °C, which was much better than the traditional BN sheets.
- ③ Crystallinity of BN. Wang et al. (2021) modulated crystallinity of BN and evaluated the catalytic performance of BN of varied crystallinity in oxidative dehydrogenation of propane. It revealed that the propane conversion rate over BN increased by about 10 times by increasing the crystallinity, gaining a propylene productivity of ~3.1 μmol g_{cat}⁻¹ s⁻¹. Characterization suggested that higher degree of crystallinity benefited the binding of O₂ to BN and the formation of active sites, which consequently resulted in a higher reaction rate.

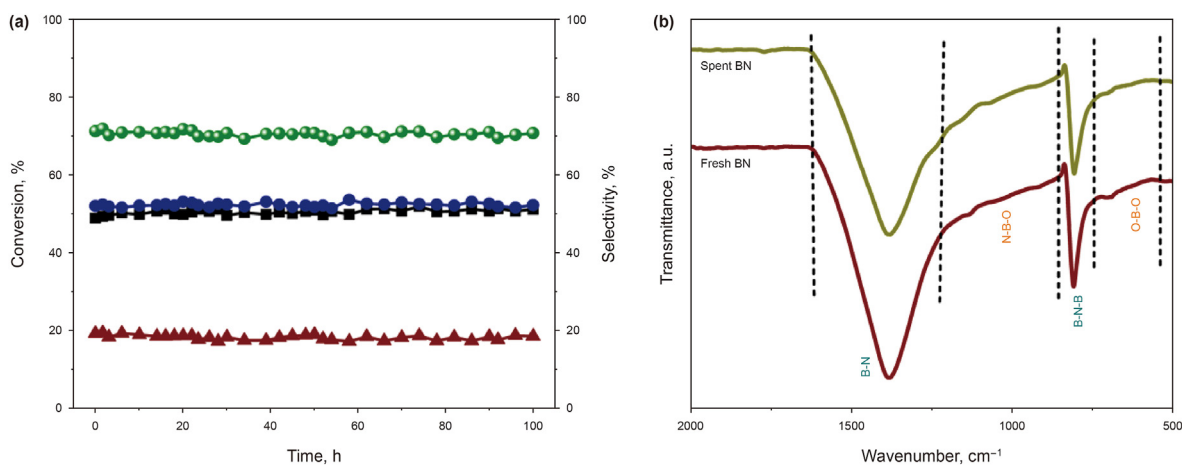


Fig. 2. (a) Stability test of BN in oxidative dehydrogenation of propane with the co-feeding of ammonia, and (b) infrared spectroscopy of fresh and spent BN. Reproduced with permission from reference (Chaturbedy et al., 2018).

④ Parameters of the reactor used for performance evaluation. As oxidative dehydrogenation of propane is exothermic, the heat and mass transfer might affect the performance of BN. Tian et al.'s study suggested that BN was of high thermal conductivity, which favored the heat transfer (Tian et al., 2018). Under the conditions that BN or $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ was evaluated in a fixed-bed reactor, the temperature gradients of catalyst bed of BN and $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ increased by $< 1^\circ\text{C}$ and $\sim 8^\circ\text{C}$, respectively, at 25.0% propane conversion and a catalyst bed diameter of 6 mm. With the increase of the catalyst bed diameter from 6 mm to 60 mm, the temperature gradient of $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst bed raised sharply (from $\sim 8^\circ\text{C}$ to $\sim 50^\circ\text{C}$), while BN could remain a relatively uniform temperature profile (Fig. 3) (Tian et al., 2018). Venegas and Hermans studied the influence of reactor parameters on the activity of BN in oxidative dehydrogenation of propane and it revealed that the transfer limitations contributed little to the observed activity. However, in the case that inert SiC was adopted as a dilute, an increase in propane conversion was obtained, which might be stemmed from the improved gas-phase chemistry (Venegas and Hermans, 2018).

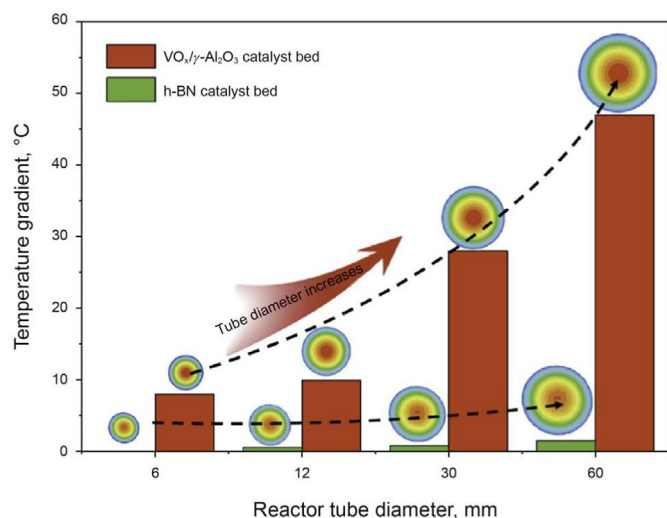


Fig. 3. Temperature gradients of BN and $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst bed with different catalyst bed diameters. Reproduced with permission from reference (Tian et al., 2018).

3.2. Oxidative dehydrogenation of propane over functionalized BN

In oxidative dehydrogenation of propane, oxygen-containing boron species (e.g., BO_x , $\text{B}(\text{OH})_x\text{O}_{3-x}$) are generally regarded as the active sites in BN. Therefore, dedicatedly introducing oxygen species into BN is a promising approach to develop BN rich in active sites that could catalyze oxidative dehydrogenation of propane effectively (Weng et al., 2016; Fukudome et al., 2011).

① Oxygen functionalized BN. Li et al. (2022) adopted a progressive substitution strategy to develop a BN catalyst with abundant O–O species. Characterization results demonstrated that there were both O–O and $\text{B}(\text{OH})_x\text{O}_{3-x}$ in the as-synthesized BN catalyst. In oxidative dehydrogenation of propane, it gave a propane conversion of 64.4% (2.8 times higher than pristine BNNT) and a total selectivity towards propylene and ethane of 48.6% at 525°C (Fig. 4). Theoretical calculation suggested that O–O species facilitated the production of propylene and ethene, while $\text{B}(\text{OH})_x\text{O}_{3-x}$ favored for propylene generation. In addition, in contrast to $\text{B}(\text{OH})_x\text{O}_{3-x}$, the synergistic effect between O–O and $\text{B}(\text{OH})_x\text{O}_{3-x}$ allowed the production of propylene via the dehydrogenation pathway at a much lower energy barrier. O–O improved the direct cracking of propane and oxidative coupling of methyl to ethene (Li et al., 2022).

Schmatz-Engert et al. (2022) adopted two strategies, calcination and ball-milling, to introduce oxide species into BN. The amount of introduced oxygen could be controlled by manipulating the calcination temperature or regulating the rotation velocity during the ball-mixing method, ranging from 0.2 to 17.5 wt%. Characterization results revealed that the introduced oxygen species existed in the form of amorphous diboron trioxide phase, which served as the catalytic active center for oxidative dehydrogenation of propane. Notably, calcined BN afforded a constant propane conversion ($\sim 25.0\%$) and a high selectivity towards propylene and ethene ($\sim 90.0\%$) (Schmatz-Engert et al., 2022).

② Edge-hydroxylated BN. Shi et al. treated BN by steam to generate B–OH groups on the edges of BN, and disclosed that the hydroxylated BN gave a superior selectivity towards propylene (80.2%) and significantly minimized CO_2 emission (0.5%) at a propane conversion of 20.6% (Shi et al., 2017a, b). The abstraction of H in B–OH groups by O_2 generated $\text{BNO}\cdot$ site, which was active for propane dehydrogenation by selectively breaking the

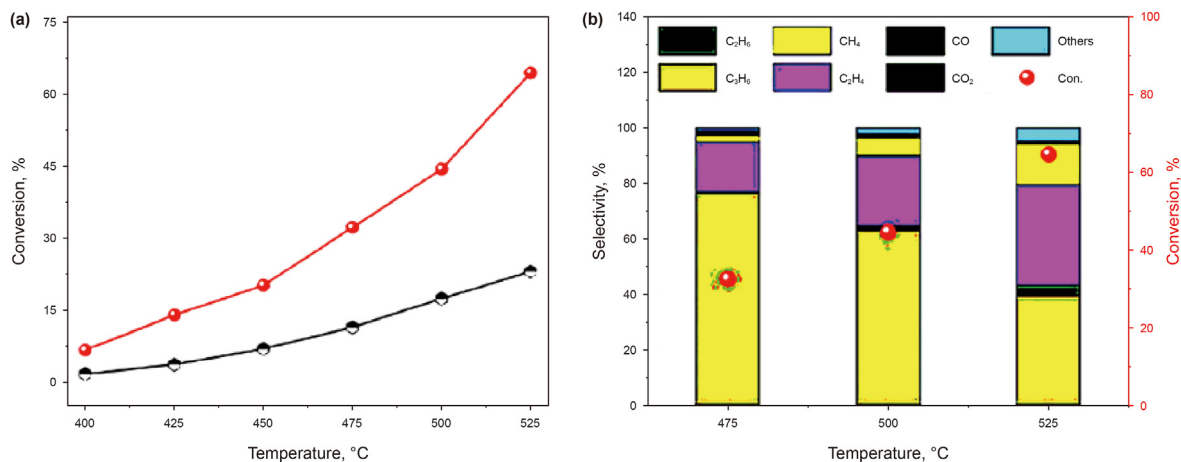


Fig. 4. (a) Catalytic activity of O–O enriched BN (red) and pristine BN (black), and (b) selectivity of O–O enriched BN in oxidative dehydrogenation of propane at different temperatures. Reproduced with permission from reference (Li et al., 2022).

C–H bond but inhibited the overoxidation of propylene to CO₂ (Shi et al., 2017a, b).

3.3. Oxidative dehydrogenation of propane over supported BN

As high heat treatment temperature is required during its synthesis process, the specific surface area of BN is generally small, which limits the number of exposed active sites on BN and consequently retards its performance in oxidative dehydrogenation of propane. Immobilizing BN onto a support of large specific surface area and excellent physicochemical properties is a promising protocol to maximize the number of active sites (Wu and Chen, 2005; Watling et al., 1996; Zhou et al., 2001).

SiO₂ is one of the promising supports for immobilizing BN, because of its good thermal and chemical stability as well as abundant –OH groups for anchoring BN. Lu et al. (2019) fabricated a BN/SiO₂ nanofiber catalyst by electrospinning the spinning solution containing exfoliated BN (rich in defects and edge sites with abundant B–OH groups) onto SiO₂ nanofiber (Chen and Chen, 2020). Due to the one-dimensional structure of SiO₂ nanofiber and the evenly dispersion state of BN, BN/SiO₂ recorded a propane conversion of 13.9% as well as a total selectivity towards propylene and ethene of 91.8% at 500 °C (Chen and Chen, 2020). Belgamwar et al. (2020) supported BN onto dendritic fibrous nanosilica (DFNS) and constructed a BN/DFNS catalyst (Fig. 5(a) and (b)). BN/DFNS gave a stable catalytic performance in oxidative dehydrogenation of propane within 20 h's life test, affording a propane

conversion of ~25.0% and a selectivity towards propylene of ~55.0% (Fig. 5(c)). Characterization results suggested that the fibrous morphology of BN/DFNS and the boron species attached to DFNS were origins of the catalytic activity (Belgamwar et al., 2020).

Cordierite is of significant advantages, such as good mass transfer, low pressure drop and narrow residence time distribution (Hensen and Green, 1973; Makino, 2007; Gibbs, 1966), which endow cordierite applicability as support for anchoring BN. Based on this, Wang and co-authors designed a BN/cordierite catalyst via a chemical deposition method (Wang et al., 2020). The good thermal conductivity of BN contributed to the heat transfer during reaction. The well-developed straight-channel of cordierite and the thin BN layer on cordierite guaranteed the efficient mass transfer even at high gas hourly space velocity (GHSV), which improved the selectivity towards propylene by suppressing secondary reactions. Overall, BN/cordierite afforded a propane conversion of ~16.8%, together with selectivities towards propylene and CO of 82.1% and 3.7%, respectively, without CO₂ being detected (Wang et al., 2020).

3.4. Oxidative dehydrogenation of propane over other BN-based catalysts

In addition to the above-mentioned strategies, several other BN-based catalysts have been developed for oxidative dehydrogenation of propane, including BN with local chemical environment regulated by plasma, doped BN catalysts, BN-based composite catalyst, BN as catalyst support, SiB₃-6 and metal borides, and etc. The progress of these BN-based catalysts for oxidative dehydrogenation

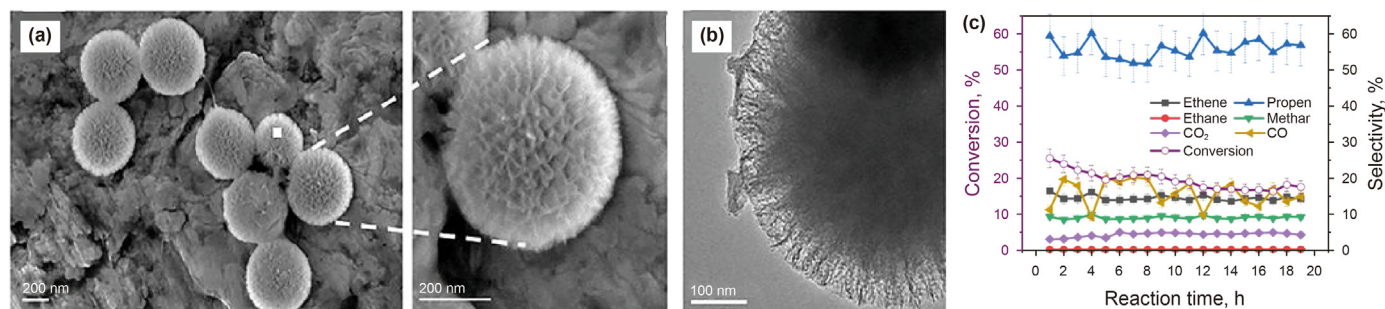


Fig. 5. (a) SEM and (b) TEM images of BN/DFNS catalyst, and (c) catalytic performance of BN/DFNS catalyst in oxidative dehydrogenation of propane. Reproduced with permission from reference (Belgamwar et al., 2020).

of propane will be illustrated below (Sheng et al., 2020; Jiang et al., 2022; Yu et al., 2016).

① BN with local chemical environment regulated by plasma.

Plasma is consisted of high energy species, which could modify the surface properties and the composition of catalysts by breaking the chemical bonds on its surface and forming new chemical bonds via the reaction with surface atoms (Zhou et al., 2018; Suzuki, 2012). Liu et al. (2021) dedicatedly treated BN by four kinds of plasma (N_2 , O_2 , H_2 and Ar plasmas), constructed boron sites with different chemical environments, and investigated the structure-performance relationships. It revealed that N_2 plasma treatment broke the chemical bonds in BN in a controlled manner and selectively abstracted the N atoms on the surface of BN, leaving more three boron center N-defects, which further evolved into BO_x and served as active sites for oxidative dehydrogenation of propane (Fig. 6) (Liu et al., 2021). As a result, the N_2 plasma treated BN exhibited a propane conversion of 26.0% and a total selectivity towards propylene and ethene of 89.4% at 520 °C. On the contrary, O_2 plasma treated BN was unfavorable for oxidative dehydrogenation of propane, probably due to the sintering of BO_x during O_2 plasma treatment (Liu et al., 2021).

② Doped BN.

Doping a foreign element into the structure of BN is an avenue to tune its physicochemical properties and consequently its catalytic performance (Guo et al., 2017). Wang et al. (2021) doped C into BN and synthesized a series of BN catalysts with tailorable C contents (Fig. 7(a)). It revealed that a suitable content of C in BN remarkably enlarged its specific surface area and enhanced the incorporation of O into BN lattice, leading to more oxygen functionalized species that were active for oxidative dehydrogenation of propane. In case that excessive C was doped into BN, the catalyst suffered from

decomposition and sintering severely, and consequently resulted in a decreased catalytic activity. The best performing catalyst exhibited a propane conversion of 18.5%, a propylene selectivity of 82.3% and a total selectivity towards propylene and ethene of 93.8% at 500 °C (Fig. 7(b)) (Wang et al., 2021).

③ BN-based composite catalysts.

Composite catalyst with multiple functions generally gives better catalytic performance than its relevant single component counterparts (Juhani et al., 2008; Chen et al., 2020). For instance, Liu et al. (2020) designed a sandwich-structured $BN@BPO_4@BN$ catalyst via an *in situ* growth method, and adopted $BN@BPO_4@BN$ for oxidative dehydrogenation of propane. In $BN@BPO_4@BN$, BPO_4 was rich in oxygen vacancies, which promoted the adsorption of propane; the space confined at the interface of BN and BPO_4 weakened the adsorption of propylene, beneficial for the regeneration of active sites. The synergistic effects between BN and BPO_4 endowed $BN@BPO_4@BN$ high activity (13.6% propane conversion) and selectivity (the selectivity towards propylene was 73.0%) in oxidative dehydrogenation of propane (Liu et al., 2020).

④ Oxidative dehydrogenation of propane over catalysts where BN is the support.

As the catalytic activity of BN in oxidative dehydrogenation of propane is generally low, introducing one or more active sites onto BN and constructing a multiple function catalyst are of great potential to realize high propane conversion (Mazzocchia et al., 1991; Grant et al., 2017; Chen et al., 2013). The application of BN as catalyst support for oxidative dehydrogenation of propane was initiated by Wu and Lin (2008). In their work, the authors prepared a Pt-Sn/BN catalyst, in which BN was considered as an inert support. They claimed that BN as support favored the formation of PtSn and $SnPt_3$ alloys, which were active in oxidative dehydrogenation

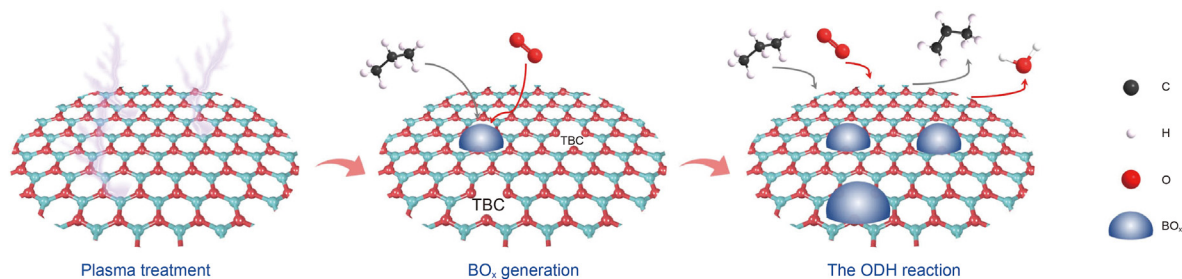


Fig. 6. Generation of three boron center N-defects during N_2 plasma treatment and its evolution into BO_x during oxidative dehydrogenation of propane. Reproduced with permission from reference (Liu et al., 2021).

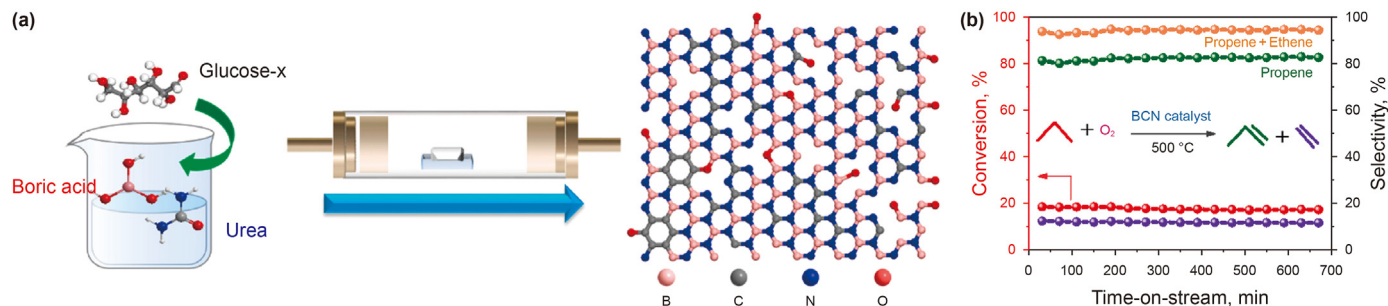


Fig. 7. (a) Schematic illustration for the synthesis of C doped BN, and (b) catalytic performance of C doped BN in oxidative dehydrogenation of propane. Reproduced with permission from reference (Wang et al., 2021).

of propane (Wu and Lin, 2008). Since the discovery of the catalytic capacity of BN in oxidative dehydrogenation of alkane, the functions of BN cannot be ignored any longer. For example, it has been reported that on Pt/BN synthesized via the impregnation method, there was a strong metal-support interaction between Pt and BN, which caused the partial encapsulation of Pt nanoparticles by BO_x layers (Wang et al., 2022). The encapsulation of Pt by BO_x constrained Pt nanoparticles into small ensembles and suppressed the cracking and dehydrogenation of propane (Wang et al., 2022).

⑤ SiB3-6 and metal borides

Boron-hyperdoped silicon catalysts, such as SiB3-6, have great potential in the oxidative dehydrogenation of propane (Chen et al., 2020). SiB3-6 realized a turnover rate of $9 \times 10^{-4} \text{ mol s}^{-1} \text{ mol}_{\text{site}}^{-1}$ at 535 °C and a selectivity towards propylene of 82.2% (the total selectivity towards ethylene and propylene reached 94.4%) (Yan et al., 2019). Over SiB3-6, the B–OH groups derived from the “BO species” might be the catalytic activity sites. In addition to boron-hyperdoped silicon catalysts, some metal borides, including NiB, Co₂B/Co₃B, TiB and WB, also showed high selectivity to propylene. The surface of these metal borides might oxyfunctionalized with the edge sites served as the active sites for oxidative

Table 1
Brief summary of BN-based catalysts in oxidative dehydrogenation of propane.

Catalyst	Preparation method	Reaction conditions	Performance	Reference
BN with larger specific surface area	High temperature calcination method	Reactor: fix-bed reactor; Catalyst dosage: 100 mg; Reactant: 10 mL min ⁻¹ 2% C ₃ H ₈ and 10 mL min ⁻¹ O ₂ ; Reaction temperature: 525 °C; Reaction pressure: 1 atm.	Propane conversion is ~50.0%, and the total selectivity towards propylene and ethene is ~70.0%.	Chaturbedy et al. (2018)
h-BN	Commercial	Reactor: fix-bed reactor; Catalyst dosage: 300 mg; Reactant: 0.15 atm O ₂ and 0.3 atm C ₃ H ₈ ; Reaction temperature: 490 °C.	Propane conversion is about 14.0% and the selectivity to propylene is ~79.0%.	Grant et al. (2016)
Spherical superstructure BN	Solvothermal transformation method	Reactor: packed-bed quartz microreactor; Catalyst dosage: 100 mg; Reactant: helium: C ₃ H ₈ : O ₂ = 4:1, totally 36 mL min ⁻¹ ; Reaction temperature: 510 °C.	Propane conversion is 58.0%, propylene yield is 27.8% and ethene yield is 12.4%.	Cao et al. (2020)
BN catalyst with high crystallinity	Calcination method	Reactor: fixed-bed quartz reactor; Catalyst dosage: 200 mg; Reactant: 23% C ₃ H ₈ , 15% O ₂ and 62% N ₂ . Totally 13 mL min ⁻¹ ; Reaction temperature: 530 °C.	The productivity of propylene is ~3.10 μmol g _{cat} ⁻¹ s ⁻¹ .	Wang et al. (2021)
BN catalyst with abundant O–O species	Progressive substitution strategy	Reactor: fixed-bed reactor; Reactant: C ₃ H ₈ /O ₂ /N ₂ with a volume ratio of 2/1/2, WHSV of 12000 L kg _{cat} ⁻¹ h ⁻¹ ; Reaction temperature: 525 °C; Reaction pressure: 0.15 MPa.	Propane conversion is 64.4%, and the total selectivity towards propylene and ethane is 48.6%.	Li et al. (2022)
Edge-hydroxylated BN	Steam activation method	Reactor: packed-bed quartz reactor; Catalyst dosage: 100 mg; Reactant: C ₃ H ₈ /O ₂ /He with a molar ratio of 1/1.5/3.5, totally 192 mL min ⁻¹ ; Reaction temperature: 560 °C; Reaction pressure: atmospheric pressure.	Propylene selectivity is 80.2%.	Shi et al. (2017)
BN/DFNS	Impregnation method	Reactor: fixed-bed reactor; Catalyst dosage: 200 mg; Reactant: 2 mL min ⁻¹ O ₂ , 2 mL min ⁻¹ C ₃ H ₈ and 8 mL min ⁻¹ N ₂ ; Reaction temperature: 490 °C.	Propane conversion is 25.0%, and the selectivity towards propylene is 55.0%.	Belgamwar et al. (2020)
BN/cordierite	Dipping method	Reactor: quartz reactor; Catalyst dosage: diameter 10 mm and length 10 mm; Reactant: 8 mL min ⁻¹ C ₃ H ₈ , 12 mL min ⁻¹ O ₂ , 28 mL min ⁻¹ N ₂ ; Reaction temperature: 510 °C.	Propane conversion is ~16.8%, and the selectivities towards propylene and carbon monoxide are 82.1% and 3.7%, respectively.	Wang et al. (2020)
N ₂ plasma treated BN	Plasma treatment	Reactor: packed-bed quartz reactor; Catalyst dosage: 100 mg Reactant: C ₃ H ₈ /O ₂ /N ₂ with a molar ratio of 1/1.5/3.5, totally 48 mL min ⁻¹ ; Reaction temperature: 520 °C; Reaction pressure: atmospheric pressure.	Propane conversion is 26.0% and the total selectivity towards propylene and ethene is 89.4%.	Liu et al. (2021)
C doped BN	In situ pyrolysis method	Reactor: fixed-bed reactor; Catalyst dosage: 50 mg; Reactant: N ₂ /C ₃ H ₈ /O ₂ with a molar ratio of 15/3/2, totally 40 mL min ⁻¹ ; Reaction temperature: 500 °C.	Propane conversion is 18.5%, propylene selectivity is 82.3% and a total selectivity towards propylene and ethene is 93.8%.	Wang et al. (2021)
BN@BPO ₄ @BN	In situ growth method	Reactor: fixed-bed reactor; Catalyst dosage: 50 mg; Reactant: 15 kPa O ₂ , 30 kPa C ₃ H ₈ , N ₂ balance, totally 20 mL min ⁻¹ ; Reaction temperature: 550 °C; Reaction pressure: atmospheric pressure.	Propane conversion is 13.6%, and the selectivity towards propylene is 73%.	Liu et al. (2020)

dehydrogenation of propane (Grant et al., 2017).

4. Summary and outlooks

To date, a number of BN-based catalysts have been developed for oxidative dehydrogenation of propane, and they could roughly be divided into pristine BN, functionalized BN, supported BN and other BN-based catalysts. Some typical examples are listed in Table 1.

From Table 1, the following research status and future prospects on oxidative dehydrogenation of propane over BN-based catalysts could be obtained.

- (1) Propane conversions over BN-based catalysts are generally low.

BN-based catalysts are highly selective for the synthesis of propylene. Over most of the BN-based catalysts, the selectivity towards propylene is > 70.0% and total selectivity towards propylene and ethene reaches ~90.0%. However, propane conversions are generally in the range of 10.0%–30.0%, which is far away from industrial application. Designing catalysts that could realize both high propane conversion and high selectivity towards propylene is one of the future research directions. Integrating BN with another active component that could dramatically accelerate the rate determining step in BN-catalyzed process might be a promising protocol to design efficient catalysts.

- (2) The stability of BN-based catalysts need improvement.

The study of BN-based catalysts in oxidative dehydrogenation of propane is still in its infant stage. Despite that some studies have evaluated the performance of BN-based catalysts for 20 or 100 h, less attention has been paid to the long-term stability of BN-based catalysts. In addition, in order to maintain the structure of BN in the oxidative dehydrogenation atmosphere, sometimes ammonia is co-fed with reactants into the reaction system. As is known, ammonia is highly corrosive. The co-feeding of ammonia raises up special requirement for the reactor. Therefore, it is urgent to develop BN-based catalysts with a long-life time that could work effectively without the co-feeding of corrosive gases.

- (3) The active sites on BN remains elusive and the reaction mechanism are still unclear.

As discussed in section 2, numerous active sites have been proposed on oxidative dehydrogenation of propane over BN-based catalysts and no consent has been reached regarding the reaction mechanism. In the future researches, more efforts should be devoted to make clear the active sites and reaction mechanism. For example, more studies should be focused on establishing the property-performance relationship, by correlating the catalytic performance of BN-based catalysts and the chemical/structural properties of the catalysts under the reaction atmosphere from the latest *in situ* characterization techniques. In addition, theoretical calculations could also be adopted, by taking all possible factors (such as reactant adsorption, intermediate formation, product desorption and etc.) into consideration, to avoid the misleading in mechanism explanation.

(4) As an emerging efficient catalyst for propane oxidative dehydrogenation, BN exhibits good propylene selectivity. Compared with the catalysts used for the Cartofin and Oleflex process, as discussed, BN has certain advantages, such as high selectivity towards olefins. Combining BN with other ingredients

could improve propane conversion and the stability of BN catalyst. It is expected that the industrialization of BN catalysts could be realized, which can even replace the existing industrial Oleflex and Cartofin processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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