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Methane activation over a boron nitride catalyst driven by in situ formed molecular water†

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Boron nitride can catalyze the oxidative conversion of methane to valuable chemicals with minor formation of CO2. B–O–H groups, both originally existing and in situ generated in the reaction, promote the activation of O2 and CH4, and a novel H2O-assisted O2 and CH4 synergetic mutual activation mechanism was proposed.

Hexagonal boron nitride (h-BN) is an emerging and revolutionary metal-free catalyst for the oxidative dehydrogenation of ethane,1 propane2 and butane,3 exhibiting higher olefin selectivity with only negligible CO2 formation compared to traditional metal-based catalysts. Actually, as a graphite-like material, h-BN with excellent structural and thermal stability4 has been widely accepted as a catalytically inert material for a quite long time.5 Thus, the activity origin of h-BN in the catalytic dehydrogenation of alkanes has aroused widespread interest. Hermans’s group proposed that oxygen-terminated armchair h-BN edges act as the catalytically active sites, and dehydrogenation occurs via the abstraction of a hydrogen atom from the secondary carbon of propane by breaking the O–O bond of >B–O–O–N–C;2b afterwards, they rediscovered the mechanism whereby surface-stabilized B2O4 sites formed under the reaction conditions act as active sites.6 Su’s group put forward a different mechanism in the dehydrogenation of ethane and they thought that the presence of ethane promoted the activation of adsorbed O2 on the edges of h-BN to form B–O(H) sites, which then abstracted hydrogen from ethane to ethene.1b In our previous work, we demonstrated that B–OH groups were generated after steam treatment of h-BN, and then the hydrogen abstraction of B–O–H by molecular oxygen dynamically generated the B–O’ sites, which triggered propane dehydrogenation by playing the role of active sites.2a Although there is a fairly clear consensus that h-BN can selectively break the C–H bond and inhibits over-oxidation of C2–C5 alkanes under an oxidative atmosphere, further study is needed to explore whether h-BN can activate more stable methane molecules and to understand the activation mechanism in-depth.

Methane, as the main component of natural gas, shale gas and gas hydrate resources, is an important feedstock for the production of value-added chemicals and fuels.7 However, the activation and conversion of methane are much more difficult and remain a great challenge due to its stable tetrahedral structure, high bond energy (434 kJ mol−1)8 and low polarizability (2.84 × 10−40 C2 m2 J−1).9 To date, the oxidative conversion of methane is mainly carried out over metal10 or metal oxide11 catalysts. The investigation of the catalytic ability of h-BN towards the activation and conversion of methane will not only result in an improved catalyst system, but also enhance our fundamental understanding in terms of the oxidative dehydrogenation ability of h-BN at the molecular level.

In this work, we demonstrated a h-BN catalyst being able to catalyze the oxidative conversion of methane and put

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Fig. 1 Selective oxidation of methane over the h-BN catalyst: a) influence of temperature on catalytic activity and selectivity, b) long-term stability test at 690 °C. Reaction conditions: catalyst, 100 mg; gas feed, 28.6 vol% CH4, 14.3 vol% O2, N2 balance; gaseous hourly space velocity 21000 mL gcat−1 h−1.
forward a novel methane activation mechanism based on the experimental and theoretical studies. The commercial h-BN was purified with NH₃H₂O and calcined in air before use. The selective oxidation of methane was performed in a packed-bed quartz microreactor under atmospheric pressure using a feed gas containing methane, oxygen and nitrogen (2:1:4). The conversion of methane is stabilized at 20.5% at 690 °C (Fig. 1a). The products include CO (76%), H₂ (14%), C₂H₄ (10%), C₂H₆ (10%), and CO₂ (4%). By raising the temperature to 720 °C, the methane conversion nearly doubled to 37.0%, while the selectivity for CO and H₂ increased slightly to 81.4% and 17.8%, respectively, and the selectivity for C₂H₄ and C₂H₆ decreased to 6.7% and 3.8%, respectively (Fig. S1†). The stability of the h-BN catalyst was tested at a constant temperature of 690 °C for 20 h. The CH₄ conversion gradually increased during the first 10 h to ∼20% and then remained stable over the entire test (Fig. 1b). No coke was detected on the catalyst after the 20 h test (Fig. S2†). By comparison, a blank experiment (a reactor with quartz sand) under the same conditions showed a CH₄ conversion of only 5.3% at 720 °C (Fig. S3†).

The origin of the catalytic performance of h-BN in CH₄ conversion was investigated first by structural analysis for fresh and spent catalysts. The surface area of fresh h-BN is 5.3 m² g⁻¹ measured by nitrogen physisorption (Fig. S4†). TEM images show a large number of edge sites. The morphology and lattice fringe are unchanged after reaction (Fig. 2a, S5†). The XRD patterns of the fresh catalyst correspond to the lattice planes of hexagonal boron nitride (JCPDS 01-073-2095). After reaction, the catalyst retains the typical hexagonal layered structure (Fig. 2b, S6†).

XPS analysis identified two types of boron species (Fig. 2c, S7†), corresponding to boron associated with nitrogen (B–N) and oxygen (B–O), respectively. Moreover, the proportion of B–O (B–O/(B–N + B–O)) increased rapidly from 0.03 in the fresh catalyst to 0.08 after 2 h and 0.13 after 9 h in the reactor (Fig. 2d), then, the proportion reached a constant value. This change is mainly attributed to the oxidation of h-BN which causes partial substitution of N by O in the h-BN lattice during the reaction.¹² Combined with the stability test result that the conversion of CH₄ gradually increased in the first 9 hours and then remained stable (Fig. 1b), we speculated that the B–O species is related to the catalytic performance.

In our previous work, we demonstrated that both B–O–B and B–O–H sites originally existed in the fresh h-BN catalyst.²⁰ To further identify which site or if both are involved in the reaction process, we first studied whether the activation of CH₄ and O₂ can be realized on the B–O–B sites by density functional theory (DFT) calculations. As displayed in Fig. S8a† if O₂ chemisorbs on the oxidized h-BN with the B–O–B terminal (Fig. S9†), its optimal adsorption energy is −2.12 eV. Such a significantly negative value of adsorption energy indicates that B–O–B could not fix O₂. Furthermore, the first C–H bond dissociation of CH₄ has to overcome the energy barrier as high as 2.29 eV, and the reaction energy of this step is evidently endothermic (Fig. S8b†). Hence, it is formidable for the B–O–B sites to activate either CH₄ or O₂ even at ∼700 °C.

We further tracked the dynamic evolution of B–O–H groups under the reaction conditions using IR spectroscopy. When exposed to a helium atmosphere, the position and intensity of the hydroxyl stretches (∼3400 cm⁻¹) are unchanged (Fig. S10a†).¹⁴ Similarly, upon exposure to a CH₄ or O₂ atmosphere, the band of the hydroxyl stretches also remains unchanged (Fig. S10b and c†). Nevertheless, when the feed gas was switched to a mixture of CH₄ and O₂, the

![Fig. 2](image-url)  
Fig. 2  a) TEM images, b) XRD patterns, c) N 1s, O 1s and B 1s XPS spectra of the fresh and spent catalysts after a 20 h test, d) influence of reaction time on the B–O proportion in B 1s XPS (B–O/(B–O + B–N)).
The intensity of the hydroxyl vibrational stretches gradually weakened (Fig. 3a).

To understand the correlation of the B–O–H with CH$_4$ activation process, we performed mass spectrometry to detect the products from the IR cell (Fig. 3b). After pulsing the mixture of CH$_4$ and O$_2$, as the absorption of the hydroxyl vibrational stretches gradually weakened, the signal intensity of CH$_4$ detected by MS gradually decreased, whereas the signal of H$_2$, CO, C$_2$H$_4$, and C$_3$H$_6$ gradually increased, demonstrating the increased conversion rate of CH$_4$ over the h-BN catalyst. Subsequently, when the hydroxyl vibrational stretches nearly remain unchanged, the signal intensity of CH$_4$, H$_2$, CO, C$_2$H$_4$, and C$_3$H$_6$ tends to reach a constant value. These results suggest that the B–O–H groups are correlated with the CH$_4$ activation assisted by oxygen.

Isotope-labelling experiments were carried out to further investigate the role of the B–O–H groups in the methane activation process. Before the test, the fresh h-BN catalyst was treated using heavy water (D$_2$O) at 590 °C. Solid-state $^1$H NMR spectra revealed that the amount of B–OH decreased after this treatment, indicating that some of the –OH groups on the catalyst were replaced by –OD (Fig. S11†). When pulsing a mixture of CH$_4$ and O$_2$ into the reaction chamber, HDO and D$_2$O were generated immediately, in addition to H$_2$O. In subsequent pulses, the intensity of HDO and D$_2$O gradually decreased while that of H$_2$O increased (Fig. 3c). In contrast, when pulsing a mixture of N$_2$ and H$_2$O, the intensity of HDO, D$_2$O and H$_2$O almost remained unchanged (Fig. S12a†), and the same result was obtained when pulsing a mixture of CH$_4$ and H$_2$O (Fig. S12b†) or a mixture of O$_2$ and H$_2$O (Fig. S12c†). These results clearly indicate that the H/D atoms in the h-BN catalyst are abstracted during the CH$_4$ conversion process rather than just re-exchanged by H$_2$O in situ generated in the reaction. It also shows that a dynamic exchange between the H atoms in the –OH groups of the catalyst surface and CH$_4$ molecule occurs during the reaction. In contrast, when only O$_2$ was pulsed in, no water isotopologs were detected (Fig. S13a†), suggesting that molecular O$_2$ cannot be activated by the surface –OH (D) groups. Similarly, no products appeared when only CH$_4$ was pulsed in (Fig. S13b†), indicating that surface –OH groups are incapable of activating CH$_4$ in the absence of O$_2$.

To further elucidate the reaction mechanism, we studied the possible reaction pathways by DFT calculations. Although it is difficult for B–O–B to activate either CH$_4$ or O$_2$, B–O–B could readily be converted to B–O–H in the presence of water (Fig. S14a†), which only needs to overcome an energy barrier of 0.67 eV for the transformation. This exothermic process releases an energy of 0.25 eV, implying a favorable transformation from B–O–B to B–O–H in the presence of water. This result is consistent with our previous work.2a Interestingly, with the formation of B–O–H, albeit still thermodynamically unfavorable, the adsorption strength of O$_2$ could remarkably be improved from −2.12 eV on B–O–B to −0.66 eV on B–O–H (Fig. S8a†), indicating the probability of forming transient intermediate O$_2$* (the asterisk denotes the surface species) on B–O–H. O$_2$ could achieve more than 1 e from BN with B–O–H (BNOH) and the O–O bond is stretched to 1.522 Å if it is chemisorbed. However, as indicated in Fig. S8b†, it is still rather drastic for BNOH to directly activate CH$_4$. The first C–H bond dissociation on BNOH has to conquer an extremely high energy barrier of 2.52 eV, which is even higher than that on B–O–B.

More interestingly, the adsorbed O$_2$ on BNOH could significantly facilitate the activation of CH$_4$. The energy barrier of the first C–H bond dissociation is dramatically reduced to 0.90 eV. After the C–H bond scission process (Fig. S14b†), the O–O bond could also be broken. Taking the effect of water for the formation of BNOH on the enhanced O–O activation into account, this sheds light on a novel H$_2$O-assisted O$_2$ and CH$_4$ synergetic mutual activation mechanism. This may be attributed to the fact that the formation of BNOH partially weakens the neighboring B–N bond strength, which makes it possible to promote the O$_2$ activation to some extent. This leads to the formation of transient surface active peroxide species which could possibly activate CH$_4$. Moreover, during the C–H bond oxidative dissociation, the obtained electrons from CH$_4$ could further activate the O–O bond, resulting in its scission (Fig. S14b†). This synergetic mechanism can explain the reason why no reaction occurs under either an independent CH$_4$ or O$_2$ flow, and also no chemisorbed species could be found after either an independent CH$_4$ or O$_2$ flow on BNOH (Fig. S15 and S16†).

The CH$_4$ and O$_2$ activation triggers the subsequent surface and gaseous radical reactions towards the formation of C$_2$H$_6$, CO, H$_2$ and H$_2$O. As depicted in Fig. 4a, at 690 °C, the

![Fig. 4. The free energy profile of a) CH$_4$ oxidation on h-BN at 690 °C, and the corresponding b) gaseous radical reactions towards CO formation at 690 °C.](image-url)
produced gaseous CH$_3^\cdot$ free radical (IS-3) could preferentially bind to the O terminal of the formed N=O bond at a low flow rate to form OCH3$^\cdot$ (IS-4) whose Gibbs free energy goes downhill by 0.74 eV. After the recovery of the B–O–B edge via hydrogen transfer and water desorption (IS-5), the broken B–N bond during O$_2$ chemisorption could be readily reformed (IS-6). Consequently, the weakening of the N–CH$_3$O bond due to the formation of the B–N bond makes CH$_3$O$^\cdot$ possible to be desorbed to form a gaseous free radical, even releasing 0.77 eV at 690 °C (IS-7). Then the remaining OH$^\cdot$ vertically adsorbed at the B site could readily activate CH$_4$ with a free energy barrier of 2.23 eV, followed by the recovery of BN from B–O–B.

During the above surface reaction cycling, two free radical species, CH$_3^\cdot$ and CH$_3$O$^\cdot$, are likely to be produced at one site, especially under the condition of a low flow rate. C$_2$H$_6$ could be readily obtained via the homocoupling of CH$_3^\cdot$. For pathway I, HCHO could be readily dehydrogenated by the O$_2^*$ adsorbed on h-BN or surface intermediate OH$^\cdot$–B (IS-7), respectively, with free energy barriers of 1.43 eV and 1.57 eV (at 690 °C). It is also very likely for the H of HCHO to be abstracted by CH$_3^\cdot$ to yield CHO$^\cdot$ at reaction pathway II, climbing uphill a free energy barrier of 1.56 eV (Fig. 4b). The similar free energy barriers indicate that once HCHO is produced, it would be subjected to deep oxidation either catalyzed by h-BN or via a gas radical reaction. The formed CHO$^\cdot$ radical is easily decomposed to CO and H$.^*$ Hence, CO is formed from the deep dehydrogenation of CH$_3$O$^\cdot$. Moreover, H$_2$ is formed via the homocoupling of H$^\cdot$ from the direct decomposition of the open-shell CH$_2$O$^\cdot$ and CHO$^\cdot$ radical. Yet due to the presence of O$_2$, the H of CHO$^\cdot$ is also likely to be abstracted from O$_2$ towards the final product H$_2$O (Table S1$^\dagger$). Since the initial formation of CH$_3$O$^\cdot$ depends on the CH$_3^\cdot$ re-adsorption on h-BN, more CO is yielded due to the higher collision possibility between CH$_3^\cdot$ and h-BN under the condition of a low flow rate while more C$_2$H$_6$ is produced under the condition of a high flow rate (Fig. S17$^\dagger$).

Conclusions

In conclusion, we have demonstrated that boron nitride can catalyze the oxidative conversion of methane to valuable chemicals, with minor formation of CO$_2$. Our experimental and theoretical studies reveal that the hydroxylated h-BN can adsorb O$_2$, and then the activation of adsorbed O$_2$ and gaseous CH$_4$ occurs through a synergetic mutual activation mechanism. The CH$_4$ and O$_2$ activation triggers subsequent surface and gaseous radical reactions towards the formation of C$_2$H$_6$, C$_3$H$_4$, CO, H$_2$, CO$_2$ and H$_2$O. This metal-free h-BN catalyst enriches our knowledge of methane activation and might lead to new possibilities for the development of more sustainable methane conversion schemes.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


