A Novel Mechanism of Activation of Methane over Metal-Free Hexagonal Boron Nitride Catalyst

Li-yang Zhao[a], Xiao-ming Cao *
[a]*Industrial Catalysis Department School of Chemistry and Molecular Engineering, East China University of Science and Technology Institution Shanghai 200237, P. R. China*
**Fax:64253755;E-mail:xmcao@ecust.edu.cn*

Abstract: Hexagonal Boron nitride (*h*-BN) is an emerging metal-free catalyst for oxidative dehydrogenation of alkanes. In this work, we demonstrated that *h*-BN catalyst be able to catalyze the oxidative conversion of methane, and a novel H_2O-assisted O_2 and CH_4 synergetic mutual activation mechanism was proposed.

Keywords: edge-hydroxylated boron nitride;methane;C-H activation

1. Introduction

Methane, as the main component of natural gas, shale gas and gas hydrate resources, is an important feedstock for production of value-added chemicals and fuels.[1] 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) and low polarizability (2.84×10^{-40} $C^2\cdot m^2\cdot J^{-1}$). Recently, it was reported that hexagonal boron nitride (*h*-BN) is an emerging and revolutionized metal-free catalyst for oxidative dehydrogenation of alkanes (including methane), exhibiting higher olefin selectivity with only negligible CO_2 formation compared to traditional metal-based catalysts. However, the catalytic active sites and the activation mechanism has not yet reached a unified understanding. Hermans's group proposed that oxygen-terminated armchair *h*-BN edges act as the catalytic 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 the >B-O-O-N<,[2] afterwards, they rediscovered the mechanism that surface-stabilized BOx sites formed at reaction conditions act as active sites[3]. Su's group put forward a different mechanism in the dehydrogenation of ethane and they thought that the presence of ethane promoted activation of adsorbed O_2 on the edges of *h*-BN to form B-O(H) sites, which then abstracted hydrogen from ethane to ethene[4]. Lu's group demonstrated B-OH groups were generated after steam treatment of *h*-BN, and then the hydrogen abstraction of B-OH by molecular oxygen dynamically generated the B-O• sites, which triggered propane dehydrogenation as active sites[5]. Hence it deserves to understand the activation mechanism in depth.

2.Computational details

The surface reaction processes were modeled based on the periodic spin-polarized density functional theory calculations utilizing the generalized gradient approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) form implemented in VASP package. The Grimme's empirical three-body dispersion correction in the scheme of Becke–Johnson dampling was also included for all the calculations to accurately describe van der Waals interaction. The electron-ion interactions were modelled utilizing the projector augmented wave (PAW) pseudopotential and the plane wave basis-set was expanded to the converged cut-off energy of 500 eV.

3. Results and discussion

Due to the discovery from Lu's group, the B-O but without N-O bond could be found during oxidation process, the reaction occurring at the oxidized BN zig-zag edge was investigated. By calculating the adsorption energy of O_2 and the energy barrier of the first C-H bond dissociation of CH_4 on the B-O-B site (Fig. 1a), we found it is difficult for B-O-B site to activate either CH_4 or O_2 (the positive value of E_{ad} suggests that the species can adsorb over the surface). 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. 1c), which only needs to overcome the energy barrier of 0.67 eV for the transformation. 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. The O-O bond is stretched to 1.522 Å. O_2 could achieve more than 1 e from BN with B-O-H (BNOH) if it chemisorbs (Fig. 1d). 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 (Fig. 1.b). After the C-H bond scission process, the obtained electrons from CH_4 could further activate O-O bond, resulting in O-O bond scission. 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_2O-assisted O_2 and CH_4 synergetic mutual activation mechanism. Followed by the first C-H bond activation, a series of surface or radical reaction could be occurred towards the formation of CO, H_2 or C_2H_6 with the different space velocities.

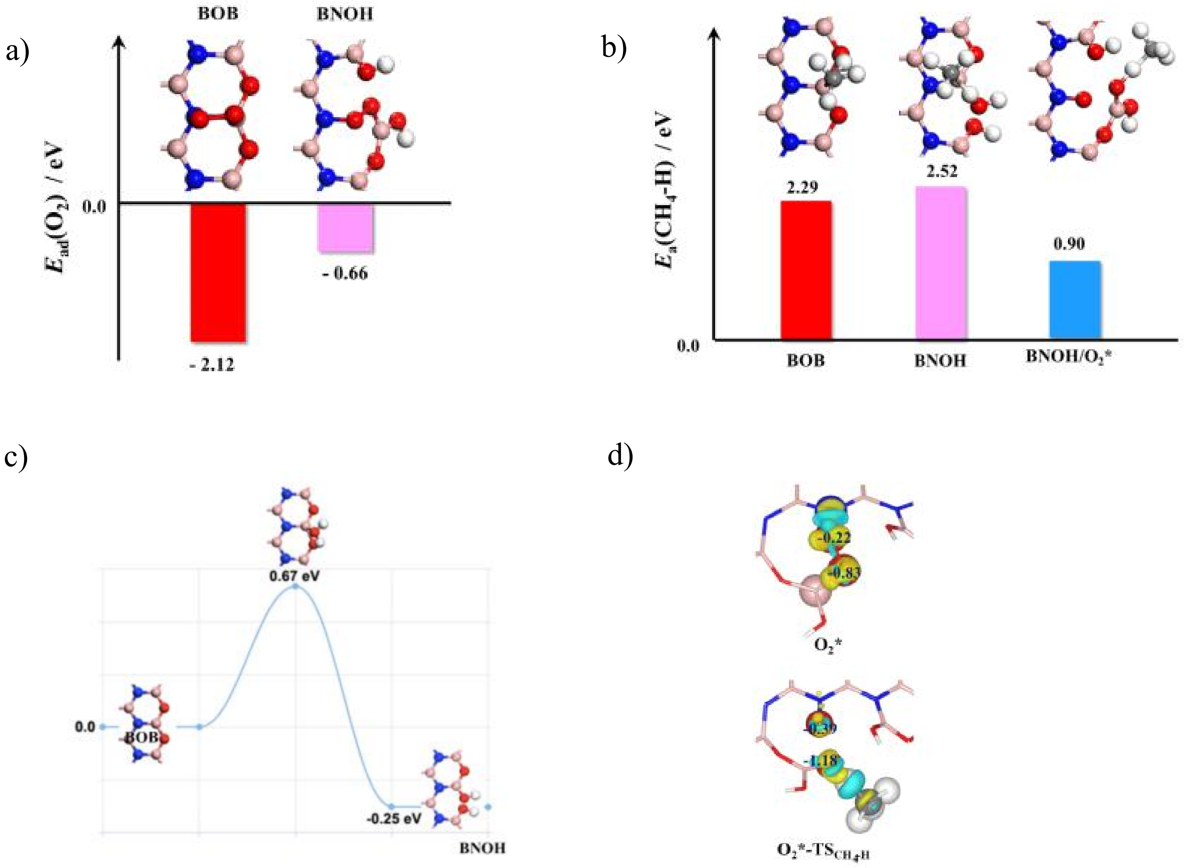

Figure 1. (a) The chemisorption energy of O_2; (b) the energy barrier of the first C-H bond scission of CH_4; (c) the energy profile of the transformation of oxidized BN to BNOH; (d) the bader charges and difference charge density of O_2* respectively during its adsorption on BNOH and the first CH_4 oxidative dehydrogenation.

Conclusions

In conclusion, our theoretical studies reveal that the edge-hydroxylated boron nitridecan adsorb O_2, and then activation of adsorbed O_2 and gaseous CH_4 occurs through a synergetic mutual activation mechanism. This mechanism could give a deep understanding of activation and conversion of CH_4 over boron nitride catalyst.

References

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