



Cite this: *Chem. Commun.*, 2021,
57, 12127

Received 8th October 2021,
Accepted 21st October 2021

DOI: 10.1039/d1cc05701d

rsc.li/chemcomm

Methane activation on dual-atom catalysts supported on graphene†

Chongchong Wu,^a Weijie Yang,^{ib} Jacky Jingyi Wang,^a Hao Li^{*c} and
Ian D. Gates^{*a}

Dual-atom Fe catalysts supported by three nitrogen atom doped graphene (Fe-TM/GP, where TM = Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) are explored for methane adsorption and activation. The addition of the second metal significantly tunes the properties of the catalysts. The main factor influencing methane adsorption is electron transfer. The second metal promotes methane adsorption by altering the electronic properties such as the band structure and charge transfer. A volcano-shaped relationship is found between the absolute value of adsorption energy and energy barrier at the heteroatom Fe-TM/GP. Fe-Ni/GP has the lowest energy barrier. Heteroatom Fe-TM/GP has a lower energy barrier than Fe-Fe/GP.

Methane, the most abundant component of natural gas, shale gas, and biogas, leads to greenhouse effects by direct emission to the atmosphere or combustion to CO₂.¹ Even worse, the greenhouse effects (*i.e.*, global warming potential) of methane are reported to be 28–36 times larger than those of CO₂ over a 100 year time period.² In addition, its low mass density under atmospheric conditions makes it challenging to store and transport methane.³ Therefore, converting methane to fuel or other chemicals is essential to utilize methane while removing greenhouse impacts. Although methane is an attractive feedstock for many high value-added products such as alcohols, alkanes, and olefins,⁴ activation of methane is extremely difficult given the stable C–H bonds, negligible electron affinity, large ionization energy, and low polarizability.⁵ Much effort has been made to explore catalysts that can directly activate methane at low temperatures.

Single-atom catalysts are attractive catalysts for methane activation owing to the strong metal–support interactions, high activity, and selectivity.⁶ Meanwhile, they have maximized utility

efficiency of metal atoms. However, the high surface energy of single-atom catalysts makes it easy to agglomerate, reducing their conversion performance.⁷ Dual-atom catalysts could prevent the agglomeration by the strong interactions between the two metal atoms.⁷ In addition, the two metals can have synergistic effects to improve the catalytic activity for reactions with bond breaking.⁸ Furthermore, dual-atom catalysts enable tuning of the adsorption properties towards a particular reactant with reduced energy input.⁹ Dual-atom catalysts exhibiting higher catalytic activity in the oxygen evolution reaction, electron reduction of ammonia, nitrogen reduction reaction, and electroreduction of CO₂ to CH₄ have been fabricated recently.^{10,11} The current techniques to synthesize dual-atom catalysts include atomic layer deposition, wet chemical adsorption, and high temperature heat treatment.¹² Fe–Co, Fe–Ni, and Fe–Cu dual-atom catalysts have been experimentally synthesized.^{12,13} Nevertheless, research on dual-atom catalysts is still emerging. As yet, no research has been reported on activating methane utilizing dual-atom catalysts.

It has been reported that the d orbitals of metals play an important role in methane activation.¹⁴ The C-p and H-s orbitals of methane can be matched and hybridized by the d orbital (d_{z²}, d_{xz} and d_{yz} orbitals) of transition metals (TMs), leading to a relatively facile adsorption and activation of methane.¹⁵ TMs such as Cr, Mn, Fe, Co, and Cu that are magnetic with partially filled d-orbitals were reported to improve catalytic activity and magnetic properties when combined with non-magnetic elements, and they have a low energy barrier for the first C–H bond activation of methane.¹⁴ Moreover, Ti, the second-most abundant transition metal with low toxicity, is an attractive metal for methane activation.¹⁶ In addition, a single V dopant has been shown to increase the stability of Rh clusters with a significantly lower energy barrier for methane activation.¹⁷ Furthermore, Ni has high catalytic activity to C–H cleavage and is widely investigated for methane activation.¹⁸ Fe is an attractive metal for methane activation and has been shown as a candidate for activating methane.^{19,20}

Here, we focus on the development of dual-atom catalysts to effectively activate methane using density functional theory (DFT)

^a Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, T2N 1N4, Alberta, Canada. E-mail: idgates@ucalgary.ca

^b School of Energy and Power Engineering, North China Electric Power University, Baoding 071003, China

^c Department of Physics, Technical University of Denmark, Lyngby, 2800, Denmark. E-mail: haoli@dtu.dk

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1cc05701d

calculations. Meanwhile, the properties of dual-atom catalysts as well as the activation mechanism will be explored. The first C–H bond activation of methane is extremely difficult and deemed as the rate-determining step for methane activation.²¹ Therefore, the initial C–H bond cleavage of methane will be investigated in detail. Our prior research has shown that a single iron atom supported on single vacancy graphene doped with three nitrogen atoms has a relatively low energy barrier for methane activation.²² Here, a second transition metal (Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) is incorporated into the single Fe doped graphene (Fe-TM/GP) to construct eight different dual-atom catalysts.

The optimized structures of the eight types of Fe-TM/GP catalysts are depicted in Fig. S1 (ESI†) with key parameters listed in Table S1 (ESI†). All the second TMs form three bonds with the three nitrogen atoms on the graphene (Fig. S1, ESI†). However, the addition of a different second TM changes the bond lengths, charges, and magnetic moments of the catalysts. The Fe–Fe length is the shortest among the Fe–TM distances and the Fe–N distance is also the shortest among the TM–N distances. The charges and charge transfer of the metals on the catalysts are all positive. As the TM changes from Ti to Cu, the charges of the TM increase. The charge transfer of the TM is positive, whereas the charge transfer of adjacent nitrogen atoms is negative, indicating that the electrons are transferred from the TM to the adjacent nitrogen atoms. In addition, the binding energy of the heteroatom Fe–TM dimer on three N atom doped graphene is larger than that of the Fe–Fe one, suggesting that there are stronger interactions between the heteroatom Fe–TM dimer and graphene supports than the Fe–Fe dimer. Overall, the shorter Fe–Fe and Fe–N distances as well as the lower binding energy of the Fe–Fe dimer on graphene than those of the heteroatom Fe–TM dimer suggest that the addition of a different TM has different influences compared with the same TM.

To analyze the stability of the catalysts, *ab initio* molecular dynamics (AIMD) simulations were conducted by using a canonical (NVT) ensemble at 298 K over 10 ps. It is shown in Fig. S2 (ESI†) that the variations of the bond lengths of Fe–N and TM–N are relatively small. This indicates that the dual-atom catalysts investigated here have high stability. In addition, projected density of states (PDOS) analysis was conducted to investigate the hybridization of the catalysts. As shown in Fig. S3 (ESI†), the p orbital of the N atom hybridizes with the d orbitals of the Fe and TM, suggesting the existence of covalent bonds between Fe/TM and N. Therefore, the Fe–TM dimer has strong interactions with the N doped graphene substrates, confirming that the dual-atom catalysts exhibit strong stability. The large binding energy suggests that the Fe–TM dimer is stably anchored on the graphene substrates. Moreover, the binding energy of the heteroatom Fe–TM dimer is more negative (*i.e.*, stronger) than that of the Fe–Fe dimer. This further suggests that the addition of a different metal will increase the stability of the catalyst. Overall, the above analysis confirms that the Fe–TM dimer is held firmly and stably on the graphene supports.

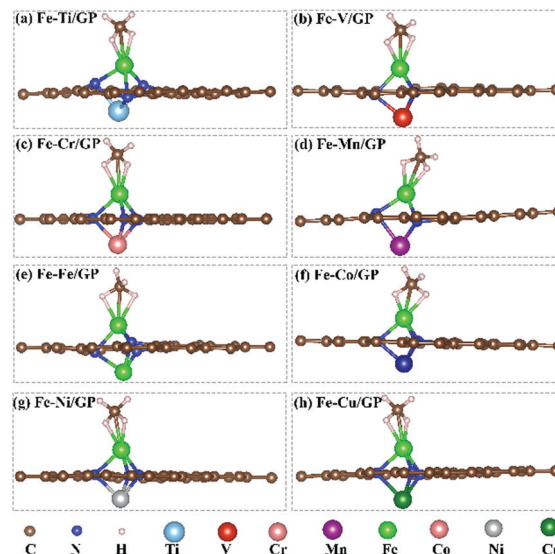


Fig. 1 Optimized adsorption geometries of methane on eight types of dual-atom catalyst.

The adsorption of CH₄ is an initial and fundamental step for methane activation on the surface of a catalyst.²³ The most stable adsorption complex of CH₄ on the dual-atom catalysts with the lowest energy is depicted in Fig. 1 with key parameters listed in Table S2 (ESI†). It is shown that CH₄ is more favorably adsorbed at the Fe site. After adsorption, the C atom and two H atoms from methane form bonds with the Fe atom, whereas the other two H atoms from methane are located further away from the catalyst surface. The elongation in C–H bond lengths is related to the dissociation of C–H. Although the C–H bond lengths of methane are altered, they do not dissociate upon adsorption. The H–C–H angle of the atoms interacting with Fe is larger than the H–C–H angle of the isolated methane, confirming that adsorption alters the structural properties of methane. When methane adsorbs on the surface of the Fe–Cu/GP catalyst, it has the largest C–H length and H–C–H angle. Different dual-atom catalysts have different Fe–C and Fe–H lengths, indicating that the addition of a second TM has a large influence on the adsorption of methane.

The adsorption energies of CH₄ on dual-atom catalysts are displayed in Fig. 2. The adsorption energies are all negative, indicating that the adsorption is exothermic and energetically favorable. If the adsorption energy is more negative than

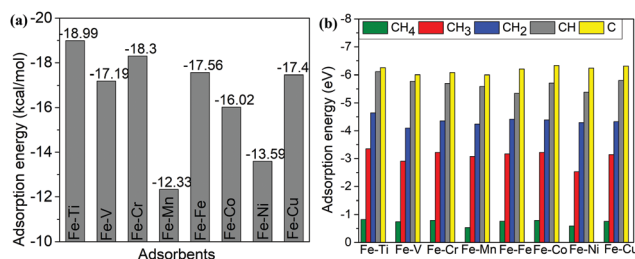


Fig. 2 Calculated adsorption energies of (a) CH₄ and (b) CH_x on dual-atom catalysts.

-16 kJ mol^{-1} ($-3.82 \text{ kcal mol}^{-1}$), chemisorption occurs.²⁴ All the adsorption energies are more negative than $-3.82 \text{ kcal mol}^{-1}$, confirming that methane is chemically adsorbed on the surface of the dual-atom catalysts. The difference of the adsorption energy confirms that the addition of the second TM affects the catalyst properties and plays an important role in methane adsorption. The adsorption energy follows the order of Fe-Ti/GP > Fe-Cr/GP > Fe-Fe/GP > Fe-Cu/GP > Fe-V/GP > Fe-Co/GP > Fe-Ni/GP > Fe-Mn/GP. Methane has the most negative adsorption energy when being adsorbed by the Fe-Ti/GP dual-atom catalyst, whereas Fe-Mn/GP has the lowest adsorption energy.

CH₄ decomposition will generate CH_x ($x = 1-3$) radicals. The adsorption energies of those radicals at dual-atom catalysts were calculated to analyze the interactions between the intermediates and dual atom catalysts (with representative structures shown in Fig. S4, ESI†). The adsorption processes of CH₃, CH₂, CH, and C involve the formation of Fe-C bonds. Different from CH₄, the H atoms of CH₃, CH₂, and CH do not form bonds with Fe. The absolute value of the adsorption energy follows the order of C* > CH* > CH₂* > CH₃* > CH₄ (see Fig. 2), indicating that C*, CH*, CH₂*, and CH₃* are more active than CH₄, consistent with a previous study.²⁵ Therefore, the current study mainly focuses on the initial C-H bond activation of methane.

Orbital hybridization and electron transfer are the two main factors affecting the adsorption of gases.¹¹ PDOS analysis after methane adsorption on Fe-TM/GP was conducted, with results shown in Fig. S5 (ESI†), to study the effect of orbital hybridization. The results show that the 1s orbital of H and the 2p orbital of C have hybridization peaks with the 3d orbital of Fe, indicating that the 3d orbital of the Fe atom hybridizes with methane. On the other hand, the p orbitals of the second TM atom do not hybridize with the 1s orbital of H and the p orbital of C, suggesting that the second TM atom does not directly take part in hybridization. The second TM atom influences the electron distribution around the Fe atom, as shown by the charge variation and bond length variation in Table S1 (ESI†), thereby influencing the adsorption and activation of methane. However, no apparent hybrid peaks exist around the Fermi level for the PDOS, indicating that hybridization does not play an important role in the adsorption of methane.

The electron density differences are plotted in Fig. S6 (ESI†) to explore the electron transfer on the adsorption of methane. Obviously, electron transfer occurs between methane and the dual-atom catalysts, suggesting that electron transfer plays an important role in the adsorption of methane. The number of electrons between C/H and Fe atoms increases, meaning that the interactions between Fe and C/H are strengthened. On the other hand, the electrons are depleted between the C and H atoms, which in turn contributes to the cleavage of the C-H bonds. The charge transfer for the adsorption of methane is listed in Table S2 (ESI†). It is shown that charge transfer for Fe and the second TM is positive, whereas it is negative for the C atom in methane, indicating that electrons are transferred from the Fe to the C atoms when methane is adsorbed. Although the second TM does not directly interact with CH₄,

electron transfer takes place and the electron transfer decreases from Ti to Cu. The electron density difference and charge transfer analysis indicate that electron transfer between methane and Fe is important for the adsorption of methane on dual-atom catalysts.

The band structures of the dual-atom catalysts and single Fe catalyst are plotted to better illustrate electron transfer in Fig. S7 (ESI†). With the addition of a second TM, the band number near the Fermi level increases and the band gap is reduced which promotes electron transfer in dual-atom catalysts and in turn improves both adsorption and catalytic activity. Therefore, electron transfer is important when adsorbing methane by dual-atom catalysts. In addition, the changes in the band structures also explain the different adsorption energy of methane with the addition of a second TM. The second TM does not take part in methane adsorption directly, but it promotes methane adsorption by changing the electron properties of the catalysts such as the valence charge and band structures. The general result is that electron transfer is the primary adsorption mechanism of methane on dual-atom catalysts.

The initial C-H bond dissociation on dual-atom catalysts was explored with transition states displayed in Fig. S8 (ESI†) and main parameters listed in Table S3 (ESI†). All of the transition states for the first C-H bond activation of methane have similar structures. Specifically, one of the H atoms on the methane molecule is abstracted by the Fe atom, leading to the formation of a Fe-H bond and breakage of a C-H bond. The Fe-C bond length is approximately 2.00 Å at the transition states, all decreasing compared to the most stable adsorption complex. In addition, the newly formed Fe-H bond distances are all longer than 1.50 Å, and they are much shorter than those of the adsorption complexes. Moreover, the dissociated C...H distances are larger than 1.50 Å, whereas the other three C-H bond distances remain approximately the same. Furthermore, the H-C-H angles are all increased compared to the most stable adsorption complex. Although the addition of the second TM does not directly lead to a bond with CH₄, the activation of the methane C-H bond alters the Fe-TM distance.

The energy barrier of the initial C-H bond activation on dual-atom catalysts, shown in Fig. 3, follows the order of Fe-Fe/GP > Fe-Ti/GP > Fe-Cr/GP > Fe-Cu/GP > Fe-Mn/GP > Fe-V/GP > Fe-Co/GP > Fe-Ni/GP. The energy barrier for Fe-Fe/GP is the largest among the catalysts investigated, which suggests that the addition of a different TM promotes the activation of methane. Therefore, the results provide an insight that the dopant of different TMs for dual-atom catalysts will benefit methane activation. In addition, Fe-Ni/GP has the lowest energy barrier among the catalysts investigated, which is only 0.23 eV (5.33 kcal mol⁻¹), much lower than that on Ni(111) (1.21 eV) and Pt(111) (1.03 eV) surfaces.²⁶ The energy barrier for the first C-H activation of methane on the dual-atom catalysts is also much lower than that on the silica-confined single-atom iron catalyst (1.80 eV)²⁷ and titanium dioxide (2.15 eV).²⁸ Moreover, the energy barrier for the initial C-H bond activation of methane on Fe-Co/GP is the second lowest. Ni and Co based

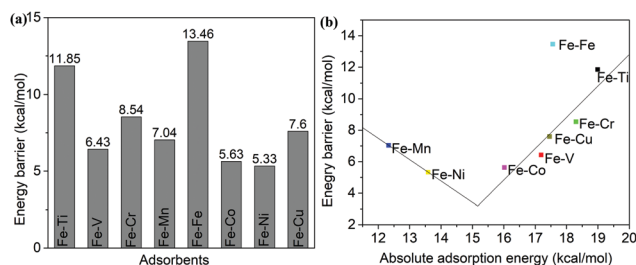


Fig. 3 (a) Energy barrier of the initial methane C–H bond activation. (b) Fitted volcano plot of the energy barrier as a function of adsorption energy.

catalysts have wide applications in dry reforming of methane.^{29,30} The calculated energy barriers on Fe–Ni/GP and Fe–Co/GP are lower than that on Cu–Ni bimetallic surfaces (12.60 kcal mol^{−1}),²⁵ implying that Fe–Ni/GP and Fe–Co/GP might be promising catalysts for the C–H bond activation of methane.

To understand the relationship between the adsorption energy and energy barrier, the energy barrier was plotted against the absolute value of adsorption energy, as shown in Fig. 3. A clear volcano-shaped relationship was found between the absolute value of adsorption energy and energy barrier for the first C–H bond activation of methane on different dual metal doped graphene. The same dual atom catalyst (Fe–Fe/GP) does not follow this trend. It is shown that the energy barrier decreases with the increase of the absolute value of adsorption energy. However, after the absolute adsorption energy reaches a certain value, the increase of the absolute value of adsorption energy leads to an increase of the energy barrier. The energy barrier is minimal when the adsorption energy is between −13.59 and −16.02 kcal mol^{−1}. The volcano plot suggests that the adsorption energy of different dual atom doped graphene should be between −13.59 and −16.02 kcal mol^{−1} to obtain the lowest energy barrier for methane activation. The relationship also makes it possible to deduce the energy barrier without calculating the transition states, thus reducing the computational cost.

DFT calculations were performed to analyze methane activation on eight types of Fe–TM/GP dual-atom catalyst. Electron transfer is the main factor influencing methane adsorption. The second metal does not directly take part in the interaction. However, it influences the adsorption by altering the band structure and electron distribution. The transition state of the initial C–H bond activation of methane involves the formation of Fe–C and Fe–H bonds. The addition of a different transition metal (TM) promotes the activation of methane. A volcano-like correlation was found between the absolute adsorption energy and energy barrier at the heteroatom Fe–TM doped graphene. The results show that Fe–Ni/GP and Fe–Co/GP, respectively, have the lowest and second lowest energy barriers for methane activation.

The authors greatly appreciate financial support from the University of Calgary Canadian First Research Excellence Fund

(entitled the Global Research Initiative in Sustainable Low Carbon Unconventional Resources).

Conflicts of interest

The authors declare that they have no competing interests.

Notes and references

- Y.-C. Liu, C.-H. Yeh, Y.-F. Lo, S. Nachimuthu, S. D. Lin and J.-C. Jiang, *J. Catal.*, 2020, **385**, 265–273.
- A. Choudhary, A. Kumar and S. Kumar, *J. Hazard., Toxic Radioact. Waste*, 2020, **24**, 06020002.
- A. S. Rosen, J. M. Notestein and R. Q. Snurr, *ACS Catal.*, 2019, **9**, 3576–3587.
- C. Choi, S. Yoon and Y. Jung, *Chem. Sci.*, 2021, **12**, 3551–3557.
- T.-H. Li, M. Yan, Y. Liu, Z.-Q. Huang, C.-R. Chang and J. Li, *J. Phys. Chem. C*, 2020, **124**, 13656–13663.
- R. Lang, W. Xi, J.-C. Liu, Y.-T. Cui, T. Li, A. F. Lee, F. Chen, Y. Chen, L. Li and L. Li, *Nat. Commun.*, 2019, **10**, 1–10.
- Y. Yang, Y. Qian, H. Li, Z. Zhang, Y. Mu, D. Do, B. Zhou, J. Dong, W. Yan and Y. Qin, *Sci. Adv.*, 2020, **6**, eaba6586.
- C.-C. Hou, H.-F. Wang, C. Li and Q. Xu, *Energy Environ. Sci.*, 2020, **13**, 1658–1693.
- X. Lv, W. Wei, B. Huang, Y. Dai and T. Frauenheim, *Nano Lett.*, 2021, **21**, 1871–1878.
- J. Zhang, Q.-a. Huang, J. Wang, J. Wang, J. Zhang and Y. Zhao, *Chin. J. Catal.*, 2020, **41**, 783–798.
- W. Yang, H. Huang, X. Ding, Z. Ding, C. Wu, I. D. Gates and Z. Gao, *Electrochim. Acta*, 2020, **335**, 135667.
- Y. Ying, X. Luo, J. Qiao and H. Huang, *Adv. Funct. Mater.*, 2021, **31**, 2007423.
- R. Yun, F. Zhan, X. Wang, B. Zhang, T. Sheng, Z. Xin, J. Mao, S. Liu and B. Zheng, *Small*, 2021, **17**, 2006951.
- S. Sahoo, S. L. Suib and S. P. Alpay, *ChemCatChem*, 2018, **10**, 3229–3235.
- X. Tang, L. Wang, B. Yang, C. Fei, T. Yao, W. Liu, Y. Lou, Q. Dai, Y. Cai and X.-M. Cao, *Appl. Catal., B*, 2021, **285**, 119827.
- P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz and L. Ackermann, *Chem. Rev.*, 2018, **119**, 2192–2452.
- T. Sengupta, J. S. Chung and S. G. Kang, *Phys. Chem. Chem. Phys.*, 2019, **21**, 9935–9948.
- M. Ouyang, P. Boldrin, R. C. Maher, X. Chen, X. Liu, L. F. Cohen and N. P. Brandon, *Appl. Catal., B*, 2019, **248**, 332–340.
- S. K. Kim, H. W. Kim, S. J. Han, S. W. Lee, J. Shin and Y. T. Kim, *Commun. Chem.*, 2020, **3**, 1–8.
- X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng and M. Wei, *Science*, 2014, **344**, 616–619.
- Y. Kwon, T. Y. Kim, G. Kwon, J. Yi and H. Lee, *J. Am. Chem. Soc.*, 2017, **139**, 17694–17699.
- C. Wu and I. D. Gates, *Mol. Catal.*, 2019, **469**, 40–47.
- T. Toyao, K. Suzuki, S. Kikuchi, S. Takakusagi, K.-I. Shimizu and I. Takigawa, *J. Phys. Chem. C*, 2018, **122**, 8315–8326.
- K. D. Pham, T. H. Ly, T. V. Vu, L. L. Hai, H. T. Nguyen, P. Le and O. Khyzhun, *New J. Chem.*, 2020, **44**, 18763–18769.
- A. Boualouache and A. Boucenna, *Chem. Phys. Lett.*, 2020, **739**, 136995.
- J. Niu, Y. Wang, Y. Qi, A. H. Dam, H. Wang, Y.-A. Zhu, A. Holmen, J. Ran and D. Chen, *Fuel*, 2020, **266**, 117143.
- Y. Liu, J. C. Liu, T. H. Li, Z. H. Duan, T. Y. Zhang, M. Yan, W. L. Li, H. Xiao, Y. G. Wang and C. R. Chang, *Angew. Chem., Int. Ed.*, 2020, **59**, 18586–18590.
- H. Song, X. Meng, S. Wang, W. Zhou, S. Song, T. Kako and J. Ye, *ACS Catal.*, 2020, **10**, 14318–14326.
- L. Azancot, L. F. Bobadilla, M. A. Centeno and J. A. Odriozola, *Appl. Catal., B*, 2021, **285**, 119822.
- S. Shah, S. Sayono, J. Ynzunza, R. Pan, M. Xu, X. Pan and K. L. Gilliard-AbdulAziz, *AIChE J.*, 2020, **66**, e17078.