Supporting information

C-H activation of light alkanes on MXenes predicted by hydrogen affinity

Kaifeng Niu^{1,2}, Lifeng Chi², Johanna Rosen¹, Jonas Björk¹

¹Department of Physics, Chemistry and Biology, IFM, Linköping University, 581 83 Linköping, Sweden

²Institute of Functional Nano & Soft Materials (FUNSOM) and Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, P. R. China

Lifeng Chi: chilf@suda.edu.cn

Jonas Björk: jonas.bjork@liu.se

Electronic structure analysis for transition states



Figure S1. Partial density of states (pDOS) of C atoms in the gas-phase propane (dashed curves), O active sites and C atoms in the transition complexes (solid curves), for dehydrogenation of the $-CH_3$ (C1) and $-CH_2$ - (C2) groups in the top and bottom panel, respectively. The vacuum level of the propane in the gas-phase has been aligned with that of the clean Ti₂CO₂ MXene without adsorbates, such that the energy difference between the vacuum and Fermi level refers to the work function of the clean MXene. The vacuum level and the Fermi level are represented by dot-dash line and the dash vertical line, respectively. The energy for the C atoms of the propane in the gas phase is given with respect to the vacuum level (upper x-axis), while the energy for the transition complexes is given relative to the Fermi level (bottom x-axis).

Figure S1 shows the pDOS of the C atoms of the propane in gas phase, the C atoms and O active sites in the transition complexes for C-H activations at C1 and C2 sites. The formation of C-O bonds at the transition complexes can be ascribed to the split of the states of the molecule in gas phase at around -7 eV with respect to the vacuum level (blue and red dash curves). Further Bader charge analysis shows that the O active sites received 0.2 electrons comparing to other O termination groups. Such results show that the charges are injected into the O active sites when C-H bonds are activated. In addition, the different bonding nature between the C1 and C2 transition complexes can be observed. As seen, the pDOS of the C2 overlap with that of O active sites at -5 eV with respect to the Fermi level. However, no featured peaks can be observed for the C1 complex. Such different bonding characteristics results in a higher stability of the C2 transition complex, leading to a lower activation energy.

The reaction pathway for the synthesis of the propylene



Figure S2. The reaction pathway of (a) two successive dehydrogenations at $-CH_{2}$ - site and (c) the synthesis of the propylene (CH₃CH=CH₂), with (b) the corresponding energy profiles. The blue and red lines represent the energy profile of the successive dehydrogenation and the synthesis of the propylene, respectively. Color code: C: brown, H: white, O: red and Ti: silver.

The abstraction of the second hydrogen atom initiates from the final state of the dehydrogenation at the $-CH_{2}$ - site, in which the 2-proxyl radical (CH₃CHCH₃) and the dissociated H atom adsorb on O termination groups, respectively. As seen in Figure S2, the successive dehydrogenation at the -CH- site exhibits a high activation energy (2.00 eV), while that for abstracting a hydrogen from a $-CH_3$ site, resulting in propylene, is 1.35 eV. Taking into account that the activation energy of the C-H activation at propane $-CH_2$ - site is 1.59 eV, the side reactions can be effectively prevented due to high activation barriers. The catalytic activity is therefore solely determined by the C-H activation at the propane $-CH_2$ - site.

The removal of H atoms on the OH terminated Ti₂C MXenes

As a natural result of dehydrogenation reactions, the OH terminations would be generated inevitably. Therefore, further investigations are focused on the removal of the OH groups in order to achieve long life cycle of the catalyst. Generally, the OH terminations can be converted into O termination by formation the H₂ molecule. Alternatively, a water molecule can be also generated from two OH groups. Figure S3 summarizes two different pathways for the removal of the OH groups. As seen, the generation of the H₂ possesses a high energy barrier, indicating that the transformation from the OH to O terminations requires high energy input (Figure 3c, orange curve). On the other hand, the formation of the H₂O is more favorable with an energy barrier of 1.32 eV. However, further calculations show that H₂O exhibits very strong interactions with the surface. The desorption of the H₂O requires an energy of 0.99 eV, while the associated formation of the H₂ from H₂O possesses a barrier of 0.80 eV. In addition, the desorption energies (E_{des}) of the H₂ and the H₂O are 0.34 eV and 2.09 eV, respectively. The desorption energy is defined as:

$$E_{des} = E_{surface} + E_{molecule} - E_{MXenes+2H}$$
(S1)

in which the $E_{surface}$, $E_{molecule}$, and $E_{MXenes+2H}$ refer to the energy of the O terminated Ti₂C, the energy of molecules in gas phase and the energy of the Ti₂C with two OH termination groups, respectively. Such highly endothermic energy suggests that the H₂O would remain at the surface after its generation. Such results indicate the H₂ is a much more likely leaving group than the H₂O. Therefore, the OH termination groups can be converted to the O active sites, agreeing well to the previous experimental observations.



Figure S3. The reaction pathways for the generation and the desorption H_2 from two OH terminations either (a) through an H_2O intermediate, or (b) directly, with corresponding energy profiles are labeled in navy and orange curves in (b), respectively. The black line refers to the desorption of the H_2O . The color code of the structures is the same as previous figures.

Furthermore, the H_2O can be generated from the dehydrogenation process of the propane molecule. As seen in Figure S4, the H_2O is formed by an OH group and the associated H atom from the 1-proxyl radical, with an energy barrier of 1.49 eV. Such barrier is higher than that of the reaction leading to the formation of two OH groups (Figure S2c), indicating that the formation of the H_2O from propane dehydrogenations is predicted to be prevented.



Figure S4. The reaction pathway and the energy profile of the generation of the H_2O from the 1-proxyl radical. The Ti, C, H and O atoms are represented by the silver, brown, white, and red circles, respectively.

Energy profile of C-H activations

Table S1. Reaction	energies (ΔE)	and activation	n energies (<i>E</i>	a) of C-H	activations at	t -CH ₃ and -	CH ₂ - groups on
Ti ₂ CO _{2-z} (OH) _z MXen	ies.						

The fraction of	CH ₃		CH ₂		
OH groups $x_{ m OH}$ (%)	ΔE (eV)	$E_{\rm a}$ (eV)	ΔE (eV)	E_{a} (eV)	
93.75	3.43	3.90	3.27	3.91	
59.38	1.91	2.63	1.83	2.44	
	3.94	3.91	3.72	4.06	
50.00	2.77	3.56	2.66	3.19	
	0.91	1.85	0.92	1.51	
	3.42	4.89	3.29	5.01	
42.75	2.67	3.92	3.45	3.87	
43.75	2.25	3.20	2.30	2.91	
	1.27	1.77	1.08	1.56	
40.63	1.17	2.03	1.20	1.69	
27.50	3.31	3.78	3.29	3.67	
57.50	2.39	2.93	2.34	2.86	
34.38	1.73	2.40	1.61	2.06	
21.25	2.94	3.33	2.65	3.15	
31.25	2.14	2.83	2.16	2.59	
	3.07	3.52	2.76	3.25	
25.00	2.52	3.33	2.72	3.21	
25.00	2.49	3.22	2.56	3.01	
	2.22	2.98	2.10	2.62	
18.75	1.92	2.64	1.80	2.33	
12 50	2.18	2.86	2.05	2.55	
12.50	1.70	2.59	1.78	2.31	
6.25	1.90	2.57	1.58	2.02	
0.00	1.27	2.01	1.09	1.60	

Table S1 summarizes the energy profile of C-H activations on selected $Ti_2CO_{2-z}(OH)_z$ MXenes. As listed, reaction energies and activation energies can be significantly different for MXenes with the same amount of OH groups. Such discrepancy indicates that the catalytic activity is not solely determined by the fraction of OH groups. Therefore, a more accurate descriptor should be introduced.

Hydrogen affinity

The hydrogen affinity is defined as:

$$E_{H} = E_{f} (M_{m} O_{x} H_{y+1}) - E_{f} (M_{m} O_{x} H_{y}),$$
(S2)

in which the $E_f(M_m O_x H_{y+1})$ and $E_f(M_m O_x H_y)$ denote the formation energies of the H absorbed catalyst and the pristine catalyst, respectively. The formation energies are defined as:

$$E_f(M_m O_x H_y) = E(M_m O_x H_y) - \left(\frac{y}{2}\right) E(H_2 O) - \left(\frac{x}{2} - \frac{y}{4}\right) E(O_2) - E(M_m),$$
 (S3)

where the $E(M_m O_x H_y)$, $E(H_2 O)$, $E(O_2)$ and $E(M_m)$ are referred to the potential energy of the O promoted catalyst, a water molecule, an oxygen molecule and the metal cluster (MXenes without termination groups in our case), respectively.^{1, 2}

Table S2. The hydrogen affinity (E_H) of Ti₂CO₂₋₂OH₂ MXenes at different H adsorption sites. Grey, red, brown, and white circles denote Ti, O, C and H atoms, respectively.

	Ti ₂ CO _{1.25} (OH) _{0.75}	Ti ₂ CO(OH)	
Top view			
Bottom view			
Average E _H (eV)	1.21	1.40	
Mean absolute error	0.005	0.003	

As it is defined, the calculation of the $E_{\rm H}$ requires the energy of the catalysts with an H atom adsorbed on. In the case of the Ti₂CO_{2-z}(OH)_z MXenes, all the terminal O groups can be considered as the possible adsorption sites of the H atom. Therefore, the influence of the adsorption sites on the $E_{\rm H}$ should be clarified. Table S2 summarizes the average $E_{\rm H}$ at different H adsorption sites on the top sides of Ti₂CO_{0.625}(OH)_{1.375} and the Ti₂CO (OH) MXenes (the fraction of OH groups are 37.5% and 50%, respectively). As listed, the mean absolute errors of the $E_{\rm H}$ with various H adsorption sites for MXenes are 0.005 and 0.003, respectively. Such small deviation indicates that the H adsorption site is not the dominant factor of the $E_{\rm H}$.



Figure S5. The hydrogen affinity (E_H) of Ti₂CO_{2-z}(OH)_z MXenes with different fractions of OH groups on the top side (x_{OH-top}) and fraction of OH groups on the bottom ($x_{OH-bottom}$) combinations. The red points are the mean E_H values for each OH group fraction combination.

The hydrogen affinities and the termination group distribution are extracted in Figure S5. As seen, the hydrogen affinity can be considered as an intrinsic property of the termination groups of the Ti_2C MXenes, in which the hydrogen affinity is solely determined by the combination of the fraction of OH groups at both sides. By extracting the fraction of OH groups into two parts, the trend between the OH group distribution and the E_H is clearly observed, in which the fraction of OH groups at the top side plays an important role in determination of the hydrogen affinity.



Figure S6. The scaling relation between the reaction energies (ΔE) and the hydrogen affinity (E_H) at (a) -CH₃ groups and (b) -CH₂- groups.

Figure S6 shows the linear correlation between the reaction energy and the hydrogen affinity for C-H activations at $-CH_3$ and $-CH_2$ - groups. As seen, the low reaction energies are observed at the MXenes with low hydrogen affinity. The catalytic activity is therefore increased as the E_H approaches to 0 eV based on the Brønsted–Evans–Polanyi (BEP) correlation.³

Reference

- 1. G. Fu, Z. N. Chen, X. Xu and H. L. Wan, Understanding the Reactivity of the Tetrahedrally Coordinated High-valence d(0) Transition Metal Oxides toward the C-H Bond Activation of Alkanes: A Cluster Model Study. *J. Phys. Chem. A*, 2008, **112**, 717-721.
- 2. A. A. Latimer, H. Aljama, A. Kakekhani, J. S. Yoo, A. Kulkarni, C. Tsai, M. Garcia-Melchor, F. Abild-Pedersen and J. K. Norskov, Mechanistic Insights into Heterogeneous Methane Activation. *Phys. Chem. Chem. Phys.*, 2017, **19**, 3575-3581.
- T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen, C. H. Christensen and J. Sehested, The Brønsted–Evans–Polanyi Relation and the Volcano Curve in Heterogeneous Catalysis. *J. Catal.*, 2004, 224, 206-217.