

# Theoretical insights into structure-reactivity relationship for C-H bond activation on rutile oxides using GBDT algorithm

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## Abstract:

In this paper, a theoretical study of C-H bond activation of methane on rutile(110), rutile(001) and rutile(011) is performed to figure out what kind of structure is suitable for this reaction. We reported a systematic investigation on reaction activation energy at different sites via energy splitting method, and we found that the coordination number of the reaction sites, the bonding direction at the transition state and the distance of the reaction sites are particularly important. Then we analyzed the importance of these features by GBDT(Gradient Boosting Decision Tree) algorithm, which shows more quantitative results for understanding structure-reactivity relationship for C-H bond activation.

**Keywords:** C-H bond activation, structure-reactivity relationship, GBDT

## 1. Introduction

C-H bond activation of methane is a key step in the catalytic conversion of low carbon alkanes in petroleum industry<sup>1, 2, 3</sup>. As a kind of catalyst with complex site structure and electronic properties, transition metal oxides have greater potential for C-H bond activation compared with metal catalysts<sup>4, 5</sup>. Liang *et al.*<sup>6</sup> found methane undergoes highly facile C-H bond cleavage on the stoichiometric IrO<sub>2</sub>(110) surface, and they emphasized the important mechanisms by which transition metal oxides with coordination of unsaturated sites. In spite of this, we still lack a comprehensive understanding of structure-reactivity relationship for C-H bond activation.

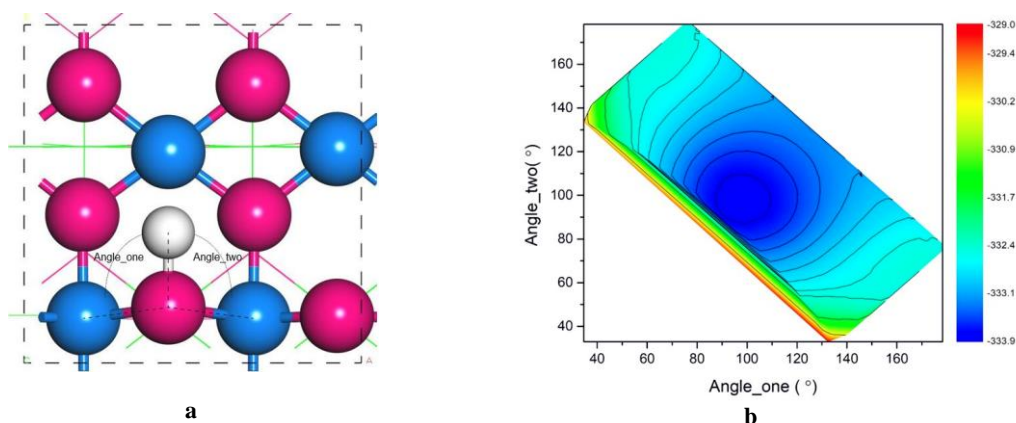
## 2. Theoretical

In our work, we have chosen eight kinds of rutile oxides, after that we mainly performed a systematic study of the first C-H bond activation of methane on rutile(110), rutile(001) and rutile(011) using DFT calculations. There are some different reactive sites on the surface, including M-O(Metal-Oxygen) and M-M(Metal-Metal) sites.

After all the transition states are found, we used energy splitting method to describe different split energy items. In order to more quantitative study the bonding direction, we deal with the data through the similarity analysis firstly, then we performed GBDT algorithm to describe the extent to which the feature affects activation energy.

## 3. Results and discussion

Let's take IrO<sub>2</sub> as an example. From activation energy in Table 1, it is clear that activation energy at M-O<sub>nn</sub>(next-nearest) site is less than M-O<sub>n</sub>(nearest) site on each surface. Moreover, M-M site is detrimental to C-H bond activation to compare to M-O site. Preliminary analysis shows the type of reaction sites, the coordination number of reaction sites and the bonding direction of the transition state maybe influence activation energy significantly. From energy map in Fig. 1b, H atom in different directions will lead to great differences in energy. Furthermore, according to these different configurations, we use the similarity analysis to quantify the angle. After that we can conclude the close relationship between these features and activation energy by GBDT algorithm.



**Figure 1.** Energy map about different bonding direction of H atom.

**Table 1.** IrO<sub>2</sub> surface structure activation energy analysis using energy splitting method.

Rutile structure	$E_a$	$\Delta H$	$\Delta E_{CH_3}^{TS}$	$\Delta E_H^{TS}$	$E_{int}^{TS}$	$\Delta E_{CH_3}^{FS}$	$\Delta E_H^{FS}$	$E_{int}^{FS}$	$d_{C-H}$	
(001)	M <sub>4</sub> -O <sub>2n</sub>	0.63	-0.97	1.62	1.4	1.06	2.02	3.01	0.65	1.408
	M <sub>4</sub> -O <sub>2nn</sub>	0.15	-0.94	1.65	1.86	1.05	1.9	3.06	0.69	1.363
(011)	M <sub>5</sub> -O <sub>2n</sub>	0.8	-0.49	1.4	1.27	1.24	1.77	2.55	0.88	1.371
	M <sub>5</sub> -O <sub>2nn</sub>	0.54	-0.36	1.29	1.67	1.21	1.74	2.56	0.77	1.331
	M <sub>5</sub> -M <sub>5</sub>	1.49	-0.39	0.96	1.47	0.79	2.03	2.63	0.44	1.45
(110)	M <sub>5</sub> -O <sub>2nn</sub>	-0.04	-1.48	1.4	1.95	1.4	2.43	3.32	0.44	1.291
	M <sub>5</sub> -O <sub>3n</sub>	0.61	-0.11	2	1.3	0.8	2.19	1.91	0.72	1.426
	M <sub>5</sub> -M <sub>5</sub>	1.03	-0.98	1.21	1.43	1.04	2.43	2.85	0.41	1.46

The energy unit is eV and the bond length unit is Å.

#### 4. Conclusions

First, M-O<sub>nn</sub> site structure is the most conducive to the first C-H activation of methane on rutile oxides. Moreover, M-O site is better for C-H bond activation of methane than M-M site on rutile oxides because of the strong interaction with CH<sub>3</sub> and H.

Second, we performed GBDT algorithm to describe the extent to which the feature affects activation energy, this result clearly shows the type of reaction sites, the coordination number of reaction sites, the bonding direction of the transition state and the distance of the reaction sites influence activation energy significantly. We make a comprehensive understanding of structure-reactivity relationship for C-H bond activation and these conclusions have guiding significance for other reactions.

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