理论计算在多相催化研究中的应用

常春然

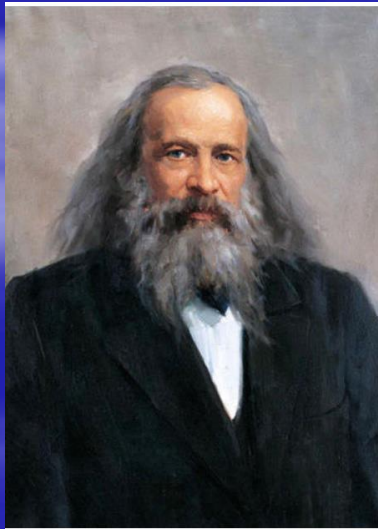**西安交通大学化工学院**

陕西省能源化工过程强化重点实验室

提 纲

一、理论与计算化学的发展历程

二、理论计算在甲烷无氧转化研究中的应用

Chemistry: An Experimental Science

- **Chemistry:**
  - The science of matter and its chemical transformation
  - alchemy, (13 century BC (商朝)~ 17 century)
  - Element --- R. Boyle (1661)
  - Chemistry: from qualitative to quantitative
    ---A. Lavoisier (1743-1794) "The father of modern chemistry"
  - Atomic Theory (J. Dalton, 1803)
  - Molecular Theory (Avogadro, 1811)
  - Periodic Table (D. Mendeleev, 1869)

Chemistry: An Experimental Science

Chemistry is primarily an experimental science, and the teaching of chemistry should be approached in an experimental vein.

---- Overview of the *New ACS Guidelines* (2000). Norman Craig (CPT Consultant)

Chemistry is an experimental science. Perhaps more than any other scientists, chemists must think with their hands. Progress in chemistry depends on the development of technique and instrumentation.

---- Review of *Instruments and Experimentation in the History of Chemistry* (2001), Jeffrey Kovac

The Scientific Method: Experiment + Theory

- **The Scientific Method**

  is the process by which scientists, collectively and over time, endeavor to construct an accurate (reliable, consistent and non-arbitrary) representation of the world.

- **Four Steps of the Scientific Method**
  - Experimentation — Observation and description of a phenomenon
  - Theorization: — Formulation of a hypothesis to interpret the phenomenon
  - Prediction: — Using the theory to predict other phenomena
  - Validation: — experimental validation of the predictions

- **Establishment of a Theory**
  - Inconsistent with expt.: rejected or modified
  - Consistent with expt.:   model or theory (law of nature)
  - Theories can never be proved, only disproved, but
    - Interpretive power
    - Predictive power

Theoretical Chemistry:
From Physics Revolution to Information Revolution
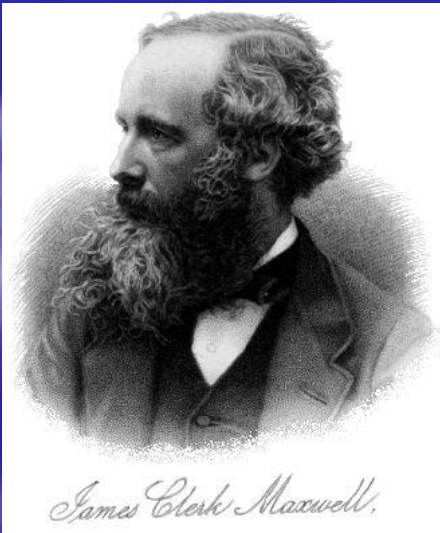
Fathers of Classic Physics

Isaac Newton (1643-1727)
discovered many of the basic rules of classic physics, including the idea of gravity:

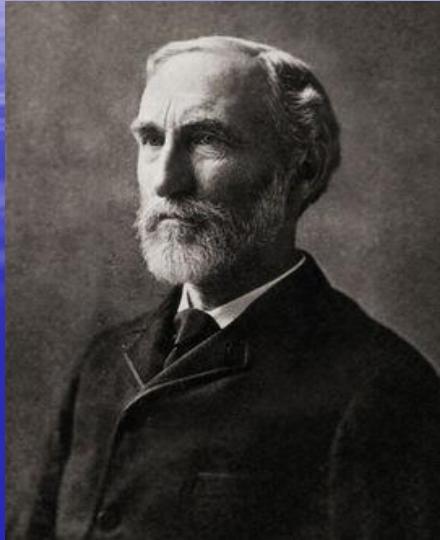$$F = ma$$
$$F = g\, m_1 m_2 \,/r^2$$

James Clerk Maxwell.

James C. Maxwell (1831-1879)
developed the basic laws of electricity and magnetism:

$$\oint_C \mathbf{E} \cdot d\mathbf{l} = -\int_{\partial C} \frac{d\mathbf{B}}{dt} \cdot d\mathbf{s}$$
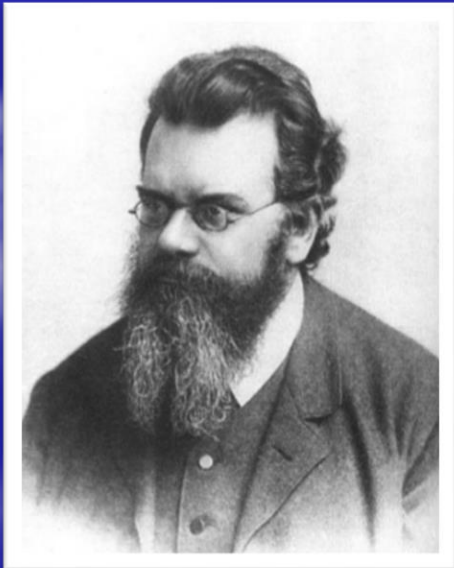
Fathers of Classic Physics

Josiah Willard Gibbs (1839-1903)
the thermodynamics he created was instrumental in transforming physical chemistry into a rigorous inductive science

$$G_{(p,T)} = H - TS$$

Ludwig Boltzmann (1844-1906)
His development of statistical mechanics which explains and predicts how the properties of atoms determine the physical properties of matter

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} + \frac{F}{m} \frac{\partial f}{\partial v} = \frac{\partial f}{\partial t}\Big|_{\text{collision}}$$

8

At the Eve of 20th Century

宣告物理学大厦已经完全建成！

"The more important fundamental laws and facts of physical science have all been discovered, and these are now so firmly established that the possibility of their ever being supplanted in consequence of new discoveries is exceedingly remote.... Our future discoveries must be looked for in the sixth place of decima"

Albert. A. Michelson(迈克耳逊)
speech at the dedication of Ryerson Physics Lab, U. of Chicago 1894

"There is nothing new to be discovered in physics now. All that remains is more and more precise measurement"

- Kelvin, Lord William Thomson
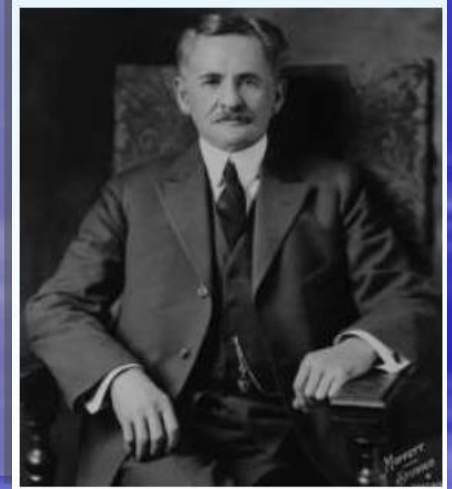
A. A. Michelson
The first American to receive Nobel Prize in Physics, 1907

# At the Eve of 20th Century

Kelvin勋爵 1900年4月27日 *(in the meeting of the Royal Institution of Great Britain)*

宣告物理学的大厦已经建成，以后只需对这座大厦作点小小的修补工作就行了；另一方面他又认为"动力学理论断言热和光都是运动的方式，可是现在，这种理论的优美性和明晰性被两朵乌云遮蔽得黯然失色了"

*... The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by **two clouds**.*

The first *came into existence with the undulatory theory of light ... it involved the question 'How could the Earth move through an elastic solid, such as essentially is the luminiferous ether?'*

The second *is the Maxwell-Boltzmann current doctrine regarding the partition of energy ...*
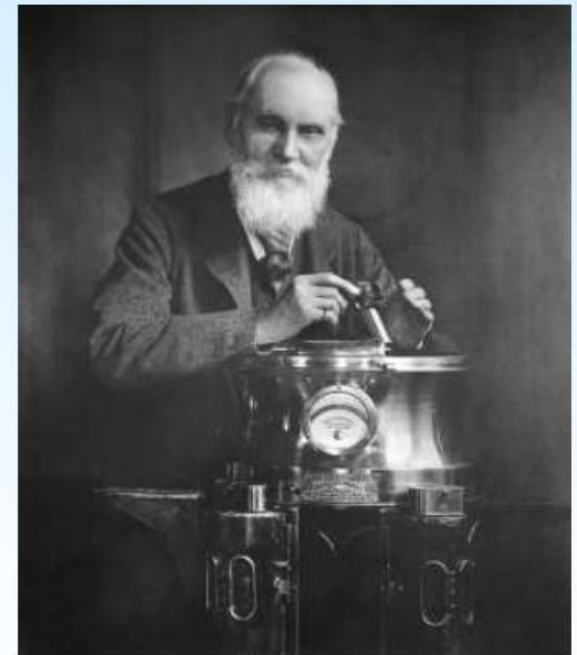
Kelvin, Lord William Thomson(1824-1907)

10

Last Two Clouds in Physics

- **Aether** (以太) **for electromagnetic field was not found …**
- **Ultraviolet catastrophe (an ideal black body at thermal equilibrium will emit radiation with infinite power): Plank 1900**

Others…
Photoelectric effect (kinetic energy of photoelectron "should be" proportional to the intensity of the light): Einstein 1905
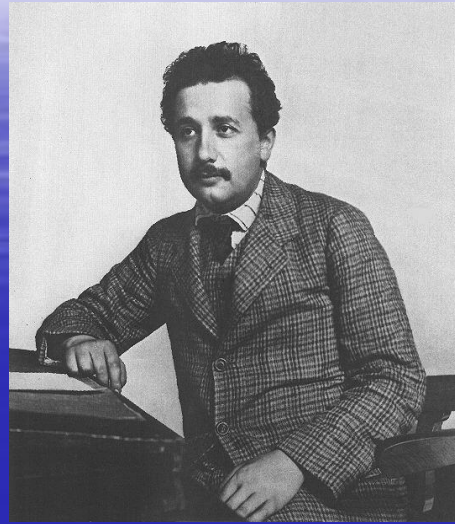
Specific heat of solids "should be" independent of temperature

Revolutions in Physics of the 20th Century:
Quantum Mechanics (1900)
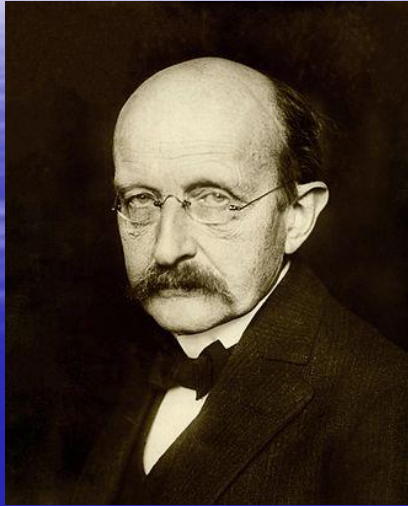
Max Planck (1858-1947)
Quantum theory (1900)
Nobel Laureate in 1918

Albert Einstein (1879-1955)
Photoelectronic effect (1905)
Nobel Laureate in 1921

Niels Bohr (1885-1962)
Bohr model of the atom (1913)
Nobel Laureate in 1922

$$E = h\nu$$

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$h\nu = E_n - E_m$$

Werner Heisenberg，Erwin Schrödinger，Louis de Broglie, Arthur Compton, Max Born, John von Neumann, Paul Dirac, Enrico Fermi, Wolfgang Pauli, Max von Laue, Freeman Dyson, David Hilbert, Wilhelm Wien, Satyendra Nath Bose, Arnold Sommerfeld, and others

Revolutions in Physics of the 20th Century:
Quantum Mechanics

20世纪物理学界最豪华的盛会

Langmuir   Plank   Curie   Lorentz   Einstein Langewin Guye Thomson Wilson

1927: The 5th Solvay Conference on Quantum Mechanics

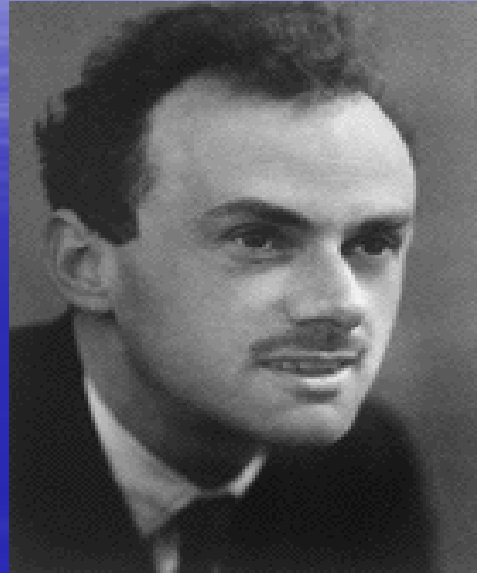# Revolutions in Physics of the 20th Century: Relativity

Albert Einstein (1879-1955), the most well-known scientist of the 20th century as the creator of special and general theories of relativity (1905）

$E = mc^2$

$$m = \frac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}} = \gamma m_0 \qquad m_0 = "rest \ mass"$$

Revolutions in Physics of the 20th Century:
Relativistic Quantum Mechanics

Paul A.M. Dirac (1902-1984)
Dirac Equation (1928)
Nobel Laureate in 1933

$$\left(\alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j p_j c \right) \psi(\mathbf{x}, t) = i\hbar \frac{\partial \psi}{\partial t}(\mathbf{x}, t)$$

Chemistry: Experiment →Theory

Vision of Dirac (aka Dirac's challenge)

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"

 —- Paul A. M. Dirac (1929)

Achievements in Theoretical Chemistry

Linus Pauling (1901-1994)

- **Nobel Prize in Chemistry 1954**
- **Nobel Prize in Peace 1962**
- **价键理论（杂化轨道）**
- **金属键理论**
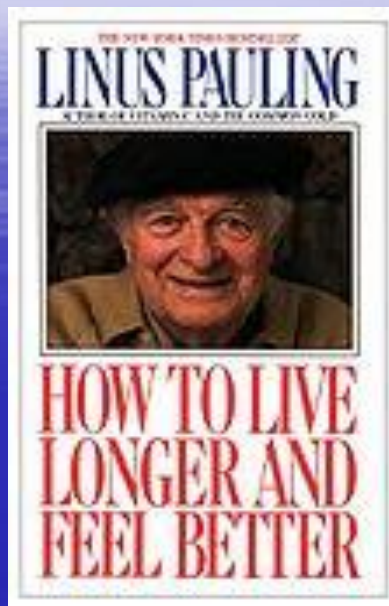
"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"

Robert S. Mulliken (1896-1986)

- **Nobel Prize in Chemistry 1966**
- **分子轨道理论(LCAO-MO)**
- **配位场理论**
- **半经验MO理论**
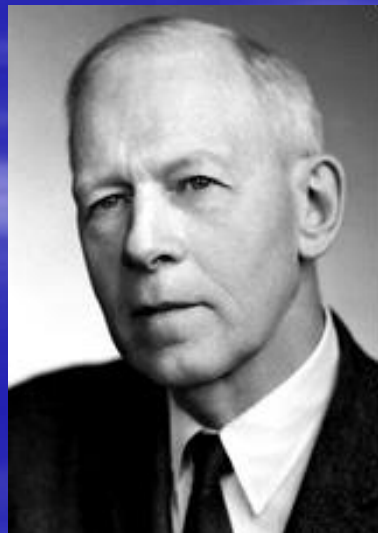
"for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method"

Achievements in Theoretical Chemistry

Fukui-Hoffmann (Nobel Prize in chemistry 1981)
前线轨道理论, 轨道对称性守恒理论, isolobal analogy

Kenichi Fukui (1918-1998)
Noble laureate in 1981 for his elucidation of the role of frontier orbitals in chemical reactions
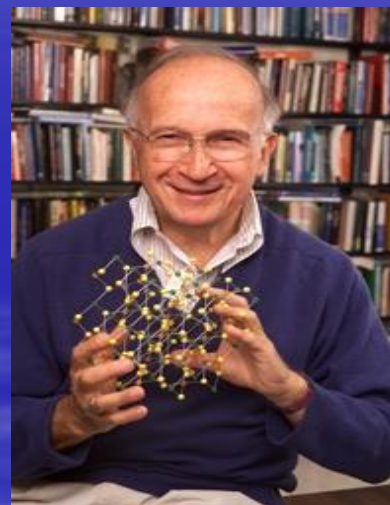
Roald Hoffmann (1937--)
Noble laureate in 1981 for the Woodward-Hoffmann rule concerning the course of chemical reactions

1966 Nobel Laureate in Chemistry: Robert S. Mulliken

"In conclusion, I would like to emphasize strongly my belief that the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand." ---R. S. Mulliken Nobel Lecture (1966)

Computational Chemistry:

An Emerging Front of Chemistry

常用的量子化学计算方法

白洽场
从头算
原子实有效势
SCF-ab initio
分子碎片法
ECP
MF
模拟从头算 SAMO
第一原理计算
浮动球
高斯法
NDDO MNDO AMI PM3
INDO MINDO
CNDO MCNDO
EHMO
IT-EHMO
C-EHMO
从头算法
Ab Initio
DV-Xα
LCAO-Xα
MSW-Xα
LCMTO-Xα
Slater Xα
半经验法
Semi-emporocal
Roothaan
方程
组态
相互作用
耦合
电子对
微扰处理
CEPA
CI
MP
独立
电子对
多组态
自洽场
MCSCF
梯度近似
局域密度
近似
LDA
GGA
密度
泛函法
DFT
Hartree-Fock
方程
IEPA
Post-HF
单电子近似
Born-Oppenheimer近似
非相对论近似
量子力学理论
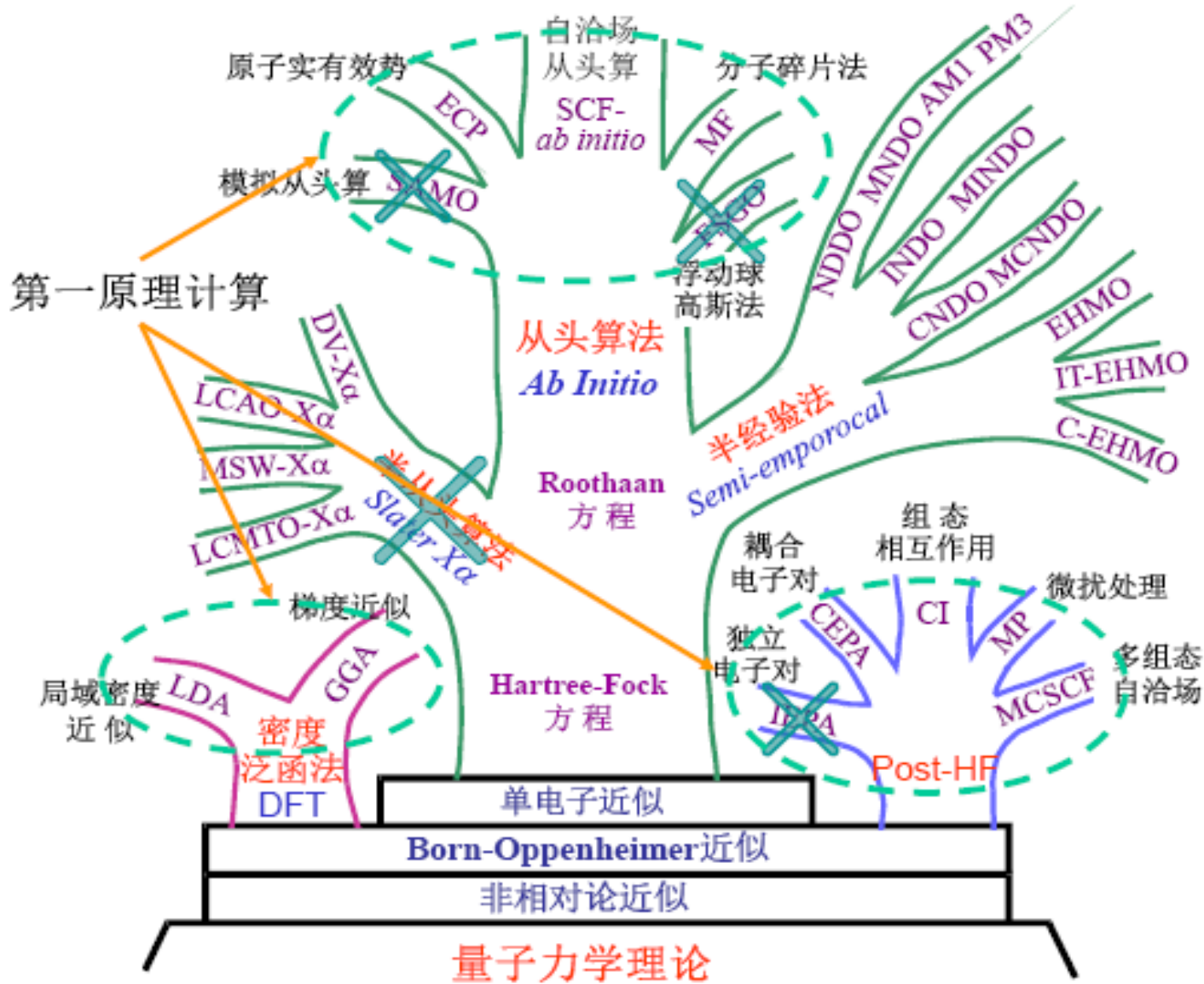
Achievements in Computational Chemistry

Kohn-Pople (Nobel Prize in Chemistry 1998)
密度泛函理论, 量子化学计算方法
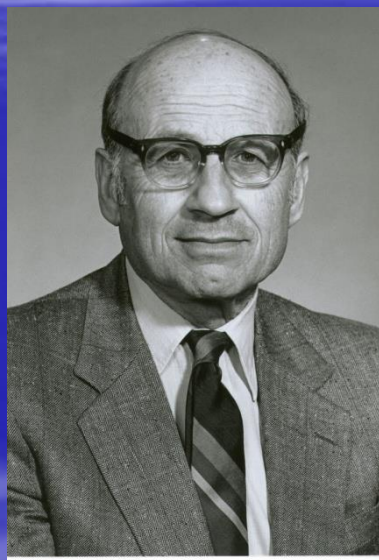
Walter Kohn (1923-2016)
Noble laureate in 1998 for his development of the density functional theory

John Pople (1925-2004)
Noble laureate in 1998 for his development of computational methods in quantum chemistry

Achievements in Computational Chemistry

Karplus-Levitt-Warshel (Nobel Prize in Chemistry 2013)
复杂化学体系的模型和计算方法

Martin Karplus (1930--), Michael Levitt (1947-), Arieh Warshel (1940-)
For the development of multiscale models for complex chemical systems

Hierarchy of Computational Methods

time

ns

ps

fs

Continuum electrostatics

MM, QM/MM, MD

SE-QM DFTB

HF, DFT

MP, CI, CC MRPT, MRCI

nm

Length scale
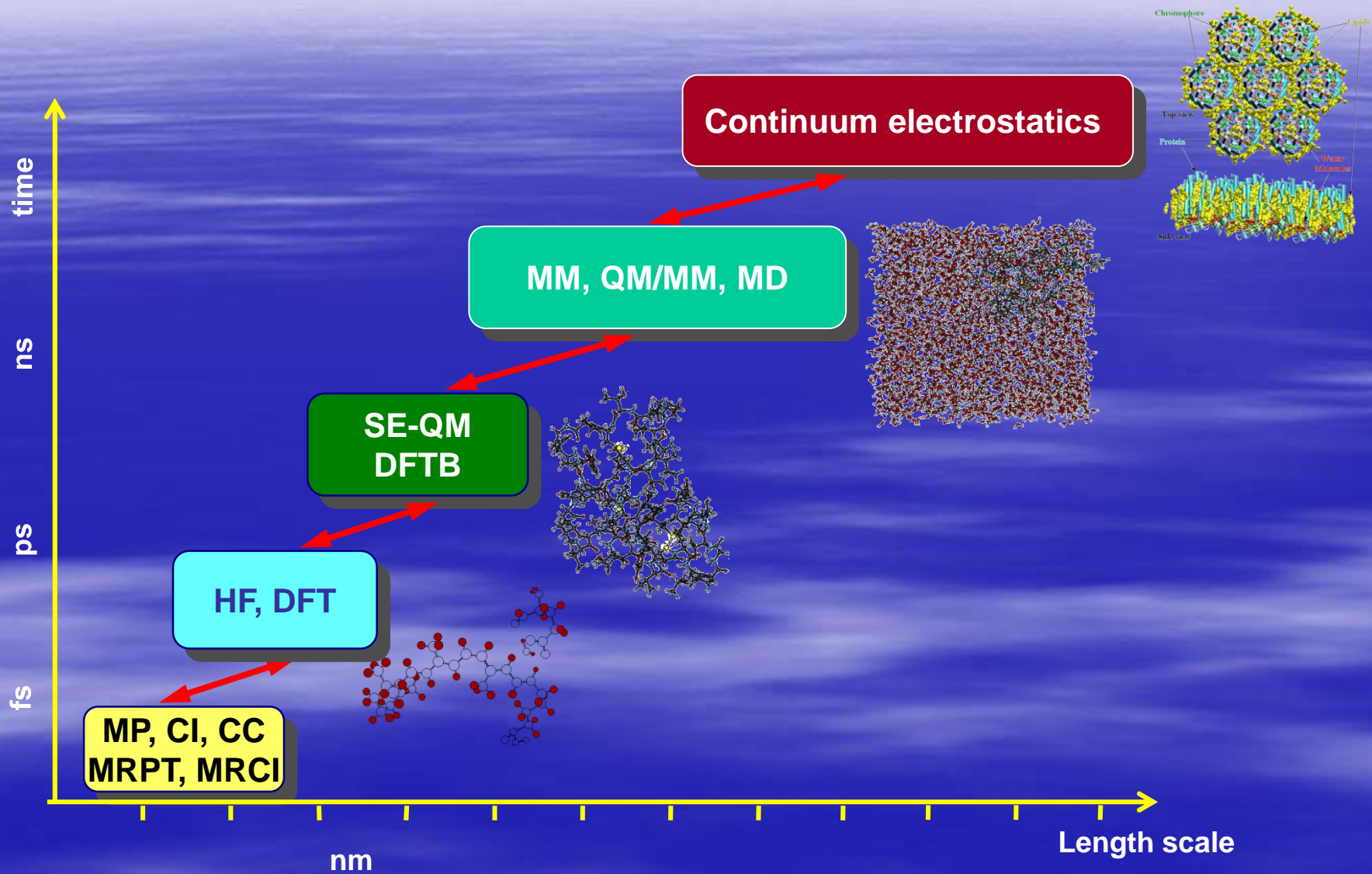
Information Revolution: Computer Era

First-ever Computer (1946): ENIAC ~ 5000 FLOPS

vs. human brain ~ 1 FLOPS

abacus ~10 FLOPS

Peta-Scale Computer Era
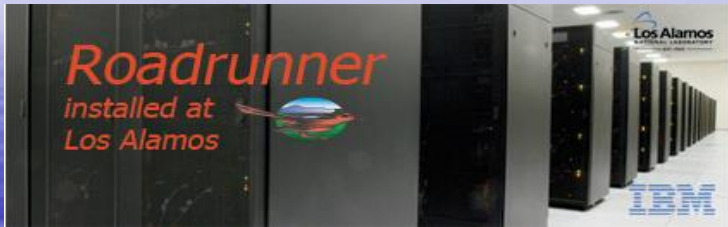
World No. 1---Tianhe-1a Computer (**2010**): 186,368 cores, **2.566×10^{15} FLOPS**

World No. 1--- K Computer (**2011**): 548,352 cores, **8.162×10^{15} FLOPS**

World No. 1 – Titan Computer (**2012**): 560,640 cores, **17.59×10^{15} FLOPS**

World No. 1 – TaihuLight Computer (**2017**): 10,649,600 cores, **93.01×10^{15} FLOPS**

World No. 1 – Summit Computer (**2018**): 2,397,824 CPU, **200.80 × 10^{15} FLOPS**

World No. 1 – Fugaku Computer (**2020**): 7,299,072 CPU, **415.53 × 10^{15} FLOPS**

World No. 1 – Fugaku Computer (**2021**): 7, 630,848 CPU, **446.01 × 10^{15} FLOPS**

World No. 4 – TaihuLight Computer (**2021**): 10,649,600 cores, **93.01×10^{15} FLOPS**

1 Sec ~ 500 million years / all the Chinese

计算科学：确保国家竞争力！

Computational Science:
Ensuring America's Competitiveness

A WAKE-UP CALL: THE CHALLENGES TO U.S. PREEMINENCE AND COMPETITIVENESS

The global information technology-powered revolution is accelerating, but this Nation has not fully awakened to the implications.   --- June 2005
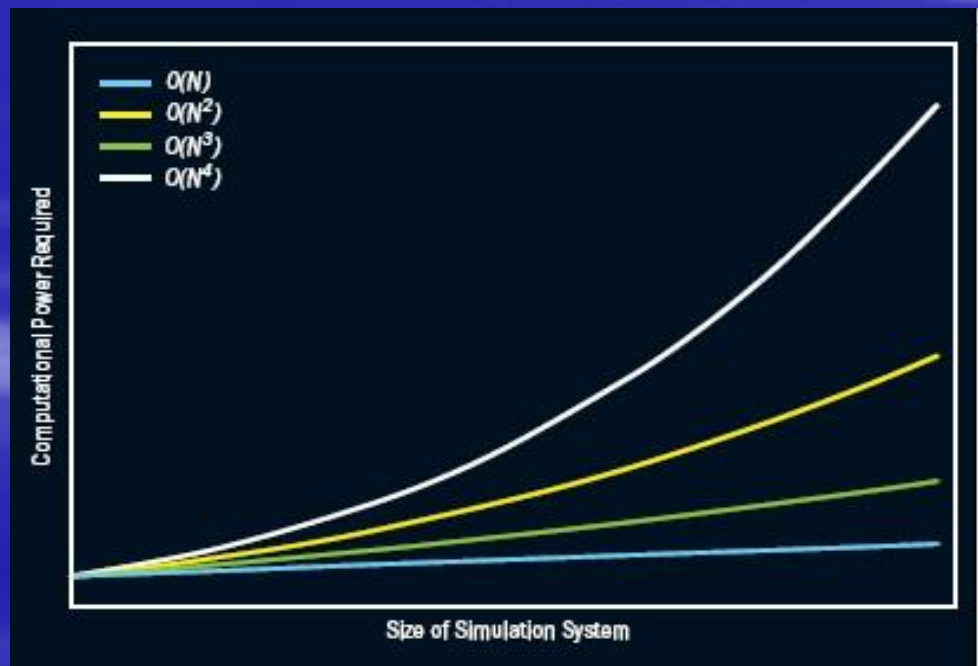
Computation: the third pillar of science

– The tools for scientific discovery in this, the 21st century, have changed. Previously, science had been limited to experiment and theory as the two pillars for investigation of the laws of nature.

– Modern computational methods are developing at such a rapid rate that computational simulation is possible on a scale that is comparable in importance with experiment and theory. The remarkable power of these facilities is opening new vistas for science and technology.

– **Ultra-Scale scientific computation adds a third pillar supporting scientific discovery to those of experiment and theory.**

   ---------- Dr. Raymond L. Orbach (Director, Office of Science, U.S. Department of Energy): *Ultra-Scale Computation and Scientific Discovery* (Nov. 2002)

Chemistry Science =
Experiment + Theory + Computation

Computational chemistry will never be able to replace experimental chemistry, but it can help to

– **interpret** experimental results,

– **predict** chemical properties, and

– **investigate** chemistry phenomena that are

  • **not easily accessible** or

  • **too expensive** for experimental research, including highly radioactive, extremely explosive, or other hazard materials, interstellar molecules, ultra-fast processes and instant species (intermediates, transition states, excited states, etc.)

提 纲

研究背景

世界能源结构变化
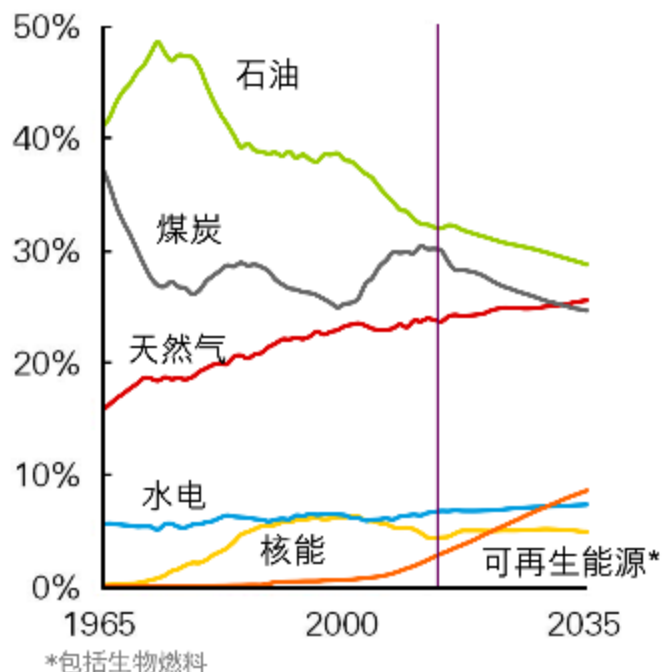
中国天然气储量丰富
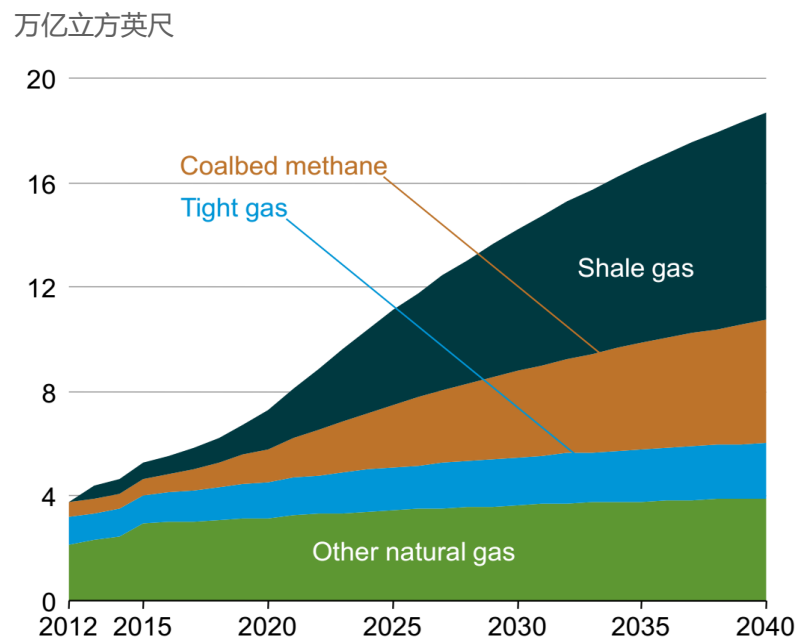
石油煤炭比重下降，天然气比重升高　　　　**我国页岩气储量30万亿立方米以上，居世界第一**

天然气的转化利用是未来解决能源环境问题的重要途径之一

* 数据来源：BP公司，《2018世界能源展望》；IEA, World Energy Outlook 2014

天然气利用的主要途径

天然气

燃烧 → 电力与供热

不足：运输成本高、附加值低

合成气 (CO + H₂)
- 甲醇 → 烯烃
- F-T 合成制油品
- 高碳化合物

不足：工艺流程复杂、目标产物选择性低

直接转化
- 选择氧化 (SOM)
- 氧化偶联 (OCM)
- 无氧转化
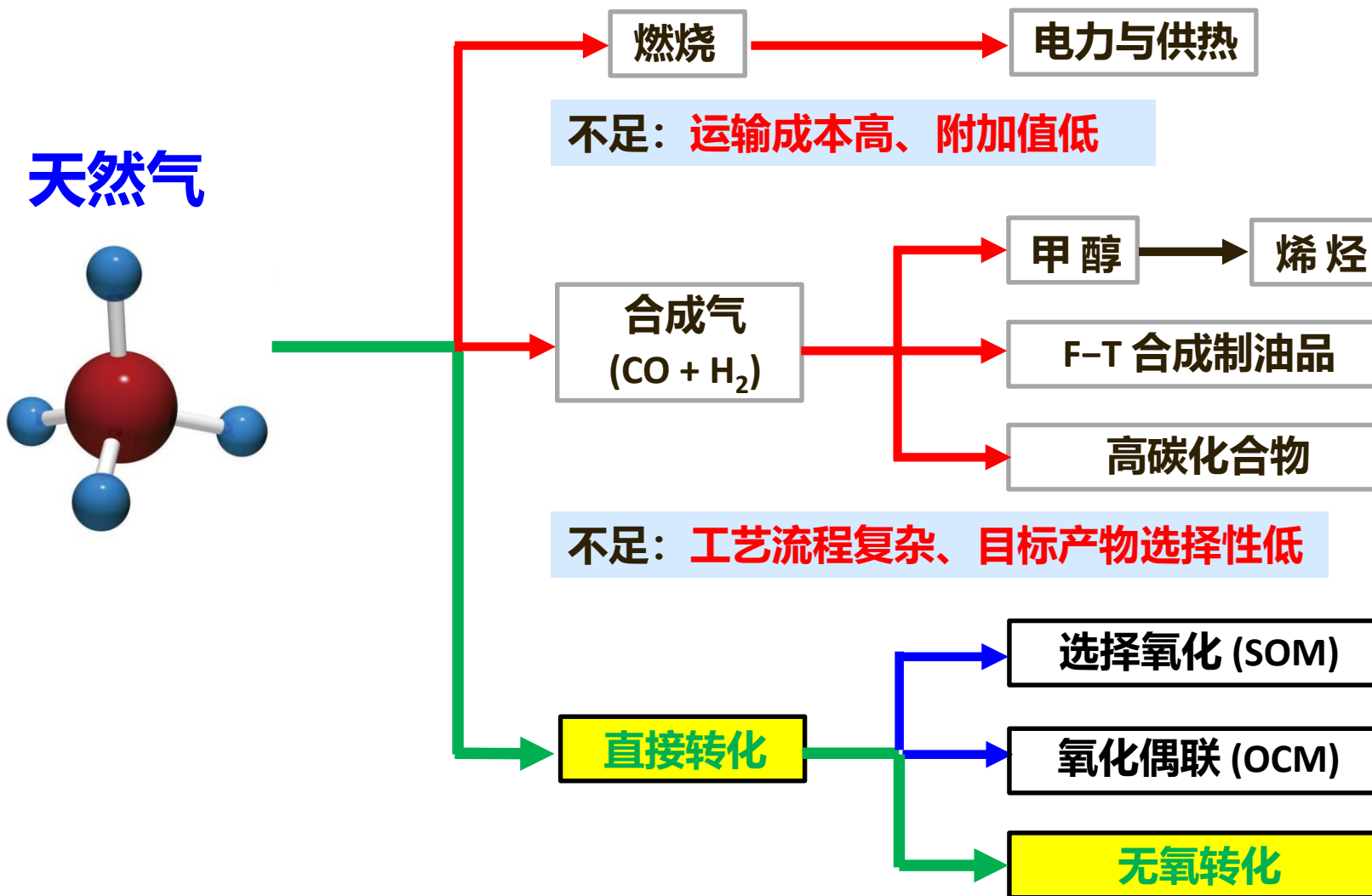
甲烷无氧直接转化的热力学分析

$$\Delta G^0_{298\,K}(2CH_4 \rightarrow C_2H_4 + 2H_2) = 169 \text{ kJ mol}^{-1}$$

$$\Delta G^0_{298\,K}(2CH_4 \rightarrow 1/3C_6H_6 + 3H_2) = 144 \text{ kJ mol}^{-1}$$
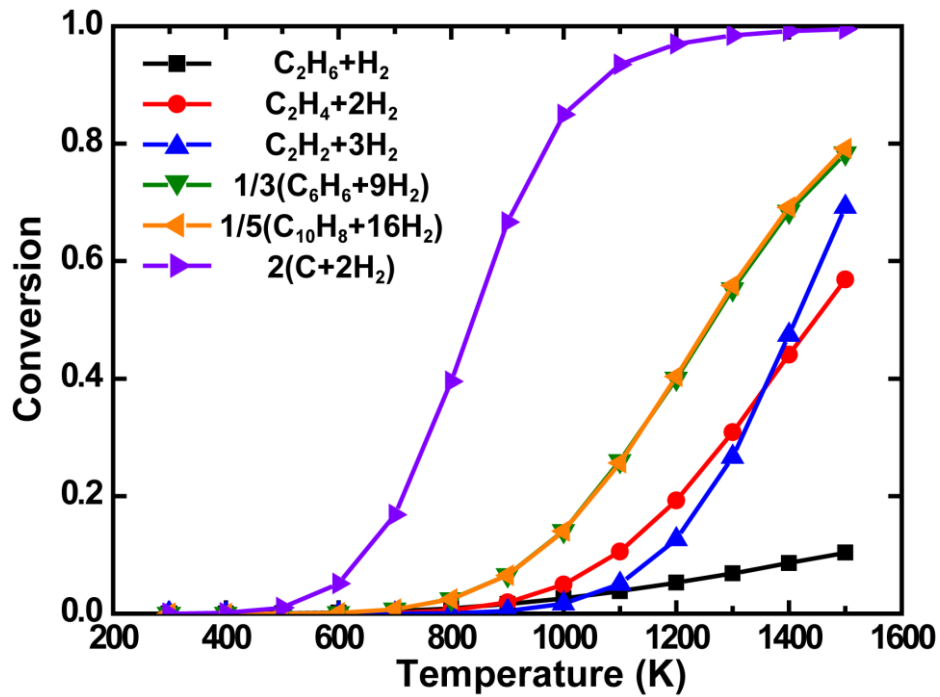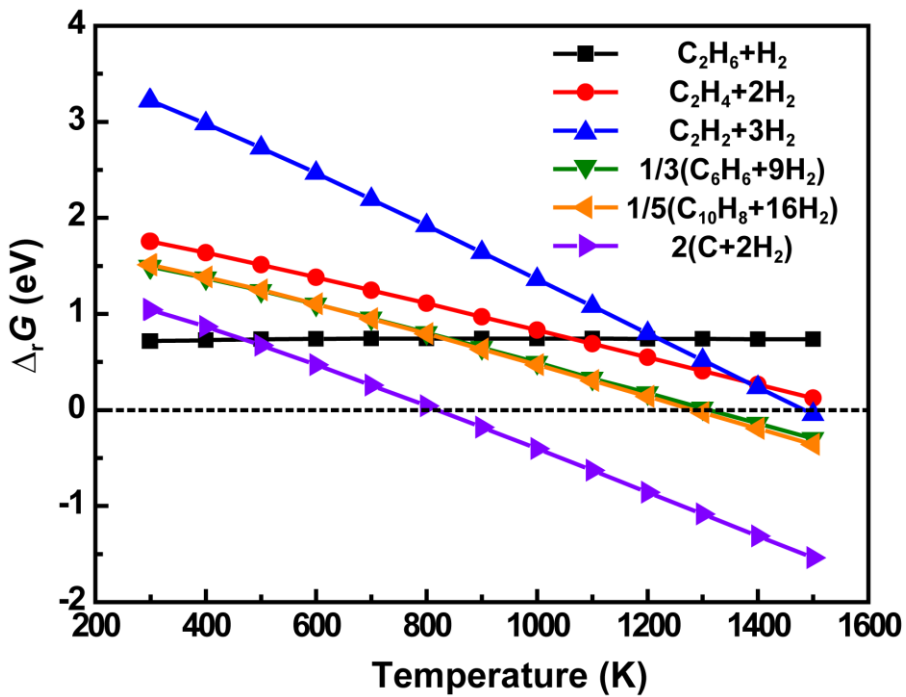
甲烷无氧直接转化的先驱工作

Conversion of methane into higher hydrocarbons on platinum

M. Belgued, P. Pareja, A. Amariglio & H. Amariglio

Pt/SiO$_2$
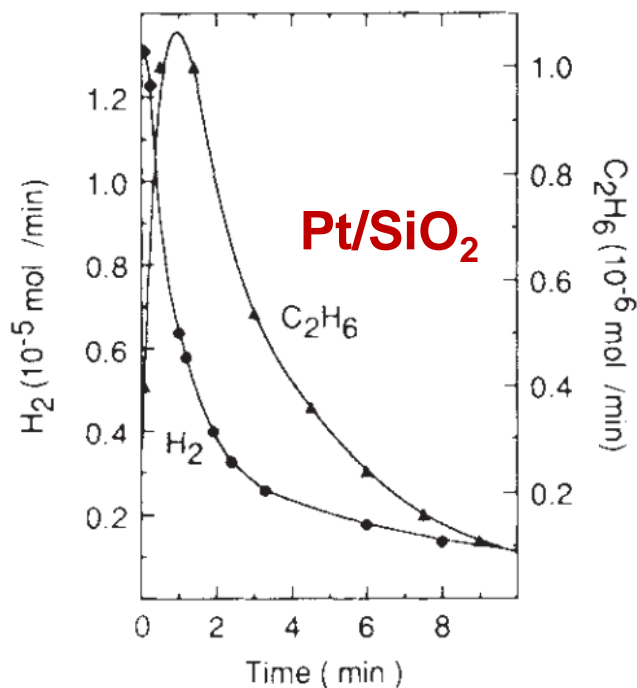
FIG. 1 Molar flow rates of H$_2$ and C$_2$H$_6$ at the exit of the reactor during the exposure of the Pt to CH$_4$ at 250 °C. Sample mass: 100 mg of EURO PT-1 (see text). Flow rate of CH$_4$: 400 ml min^{-1} under ordinary pressure.

*M. Belgued, et al., Nature, **1991**, 352, 789.*

Dehydrogenation and aromatization of methane under non-oxidizing conditions

Linsheng Wang, Longxiang Tao, Maosong Xie, Guifen Xu
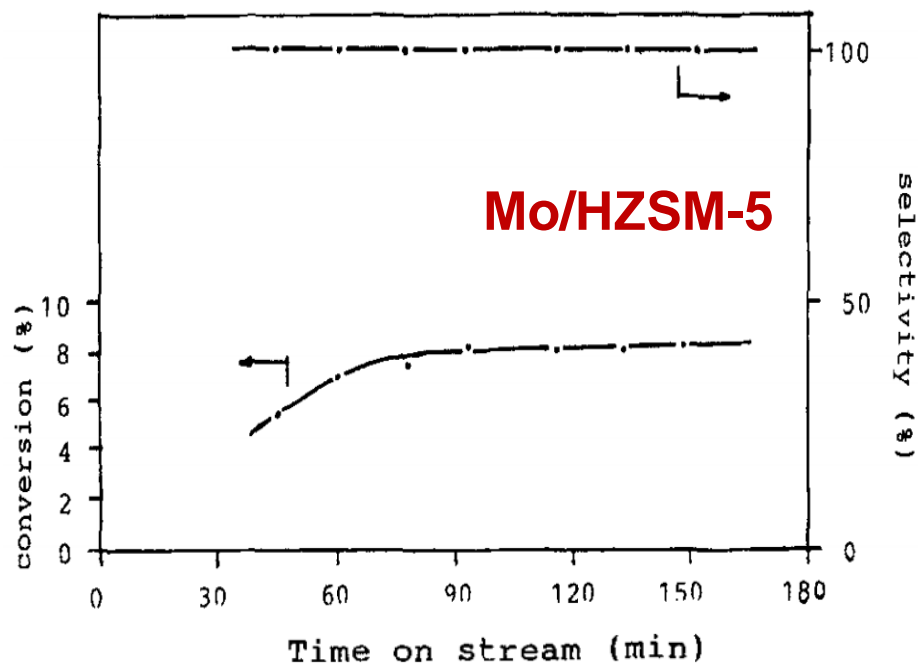
Mo/HZSM-5

FIG. 2. The change in activity with time of the MoHZSM-5 catalyst for the aromatization of methane.

*L. Wang, et al., Catal. Lett. **1993**, 21, 35.*

晶格限域的**单铁中心**催化甲烷无氧转化
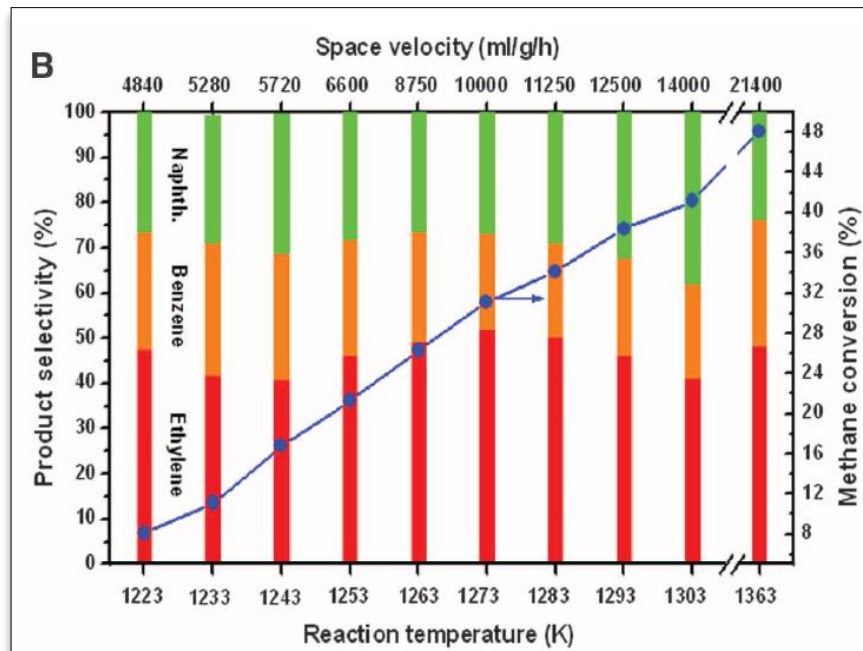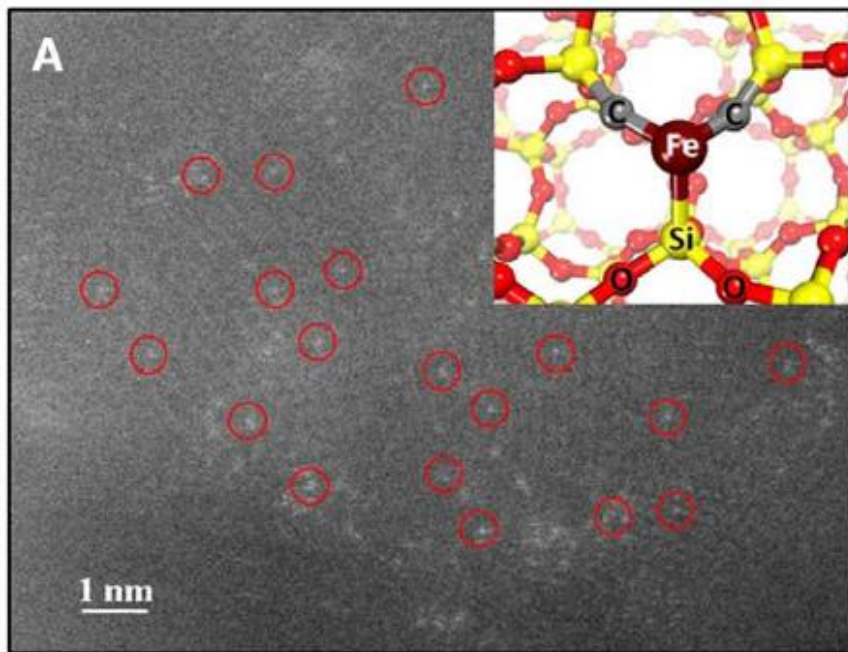
X. Guo,…, X. Bao, *Science* 2014, *344*, 616

高转化率(48.1%), 高烯烃、芳烃选择性(>99%), 无积碳, 零CO₂排放!

国际天然气转化委员会主席Prof. K. de Jong: 该工作是近百年来碳一催化概念的一个重要突破，必将会引领该领域发展的新方向!

拟解决的关键科学问题

技术瓶颈

反应温度较高(>1300 K)

催化剂的高温长时稳定性、

及整体催化效率有待提高
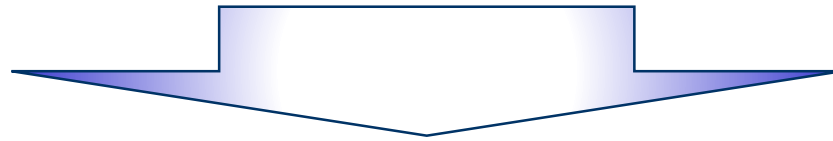
关键科学问题

单铁中心的形成机制

单铁中心催化甲烷无氧转化的动态机理

新型单/多中心催化剂的设计及构-效关系

研 究 成 果
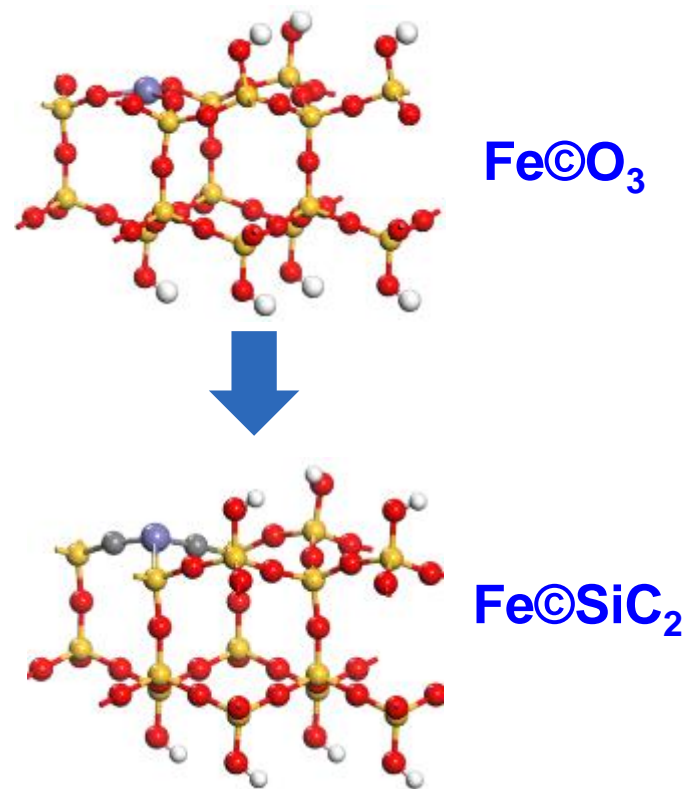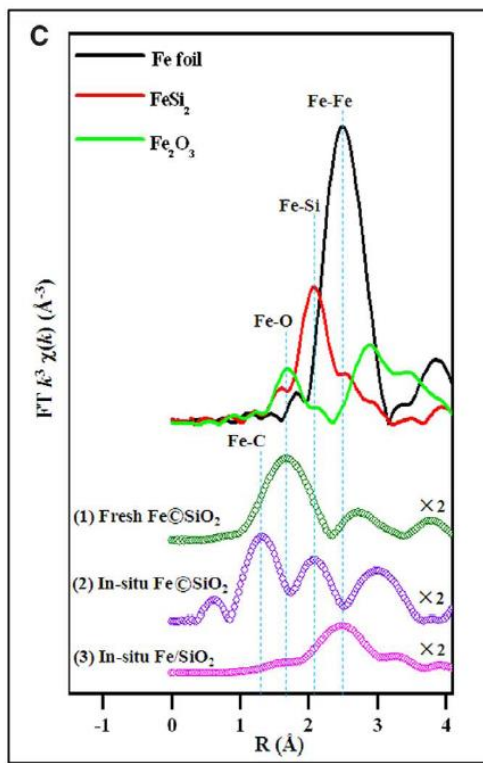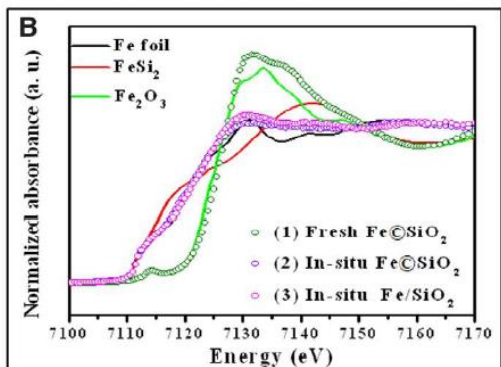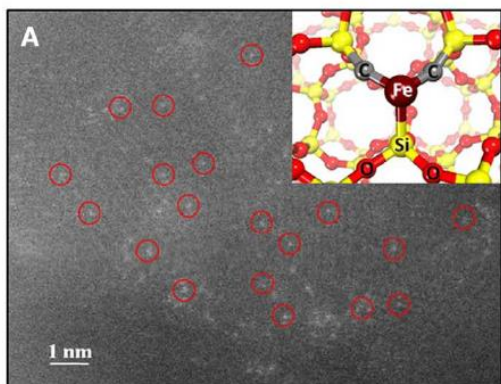
□ **Raw materials for catalyst: ferrous metasilicate, SiO$_2$, air, HNO$_3$ for leaching**

□ **Fresh catalyst: no Fe-Fe bonds, Fe-O bonds are dominant**

□ **In-situ catalyst: no Fe-Fe bonds , Fe-O disappears, Fe-C and Fe-Si appear**

X. Guo, X. Bao*, et al., Science 2014, 344, 616.

Fe©O₃   Fe©SiC₂

$$CH_4 + O^* \rightarrow CH_2 + H_2O \rightarrow C^* + H_2 + H_2O$$
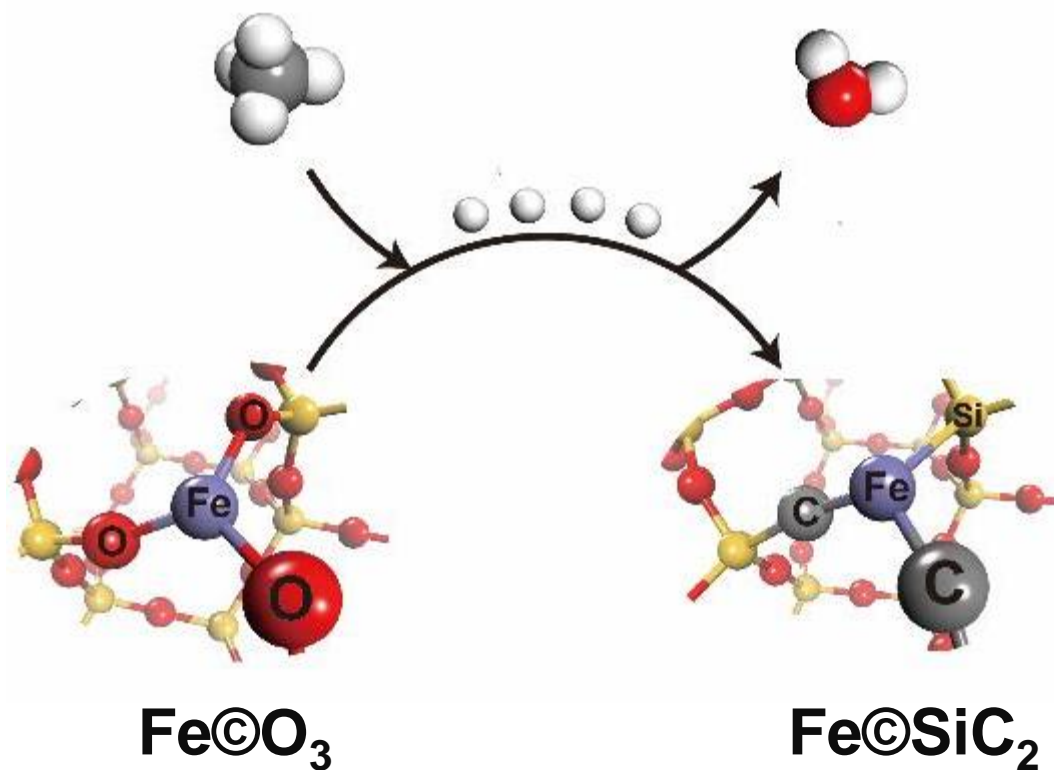
在甲烷分解H的作用下 Fe©O₃ 到 Fe©SiC₂的演变
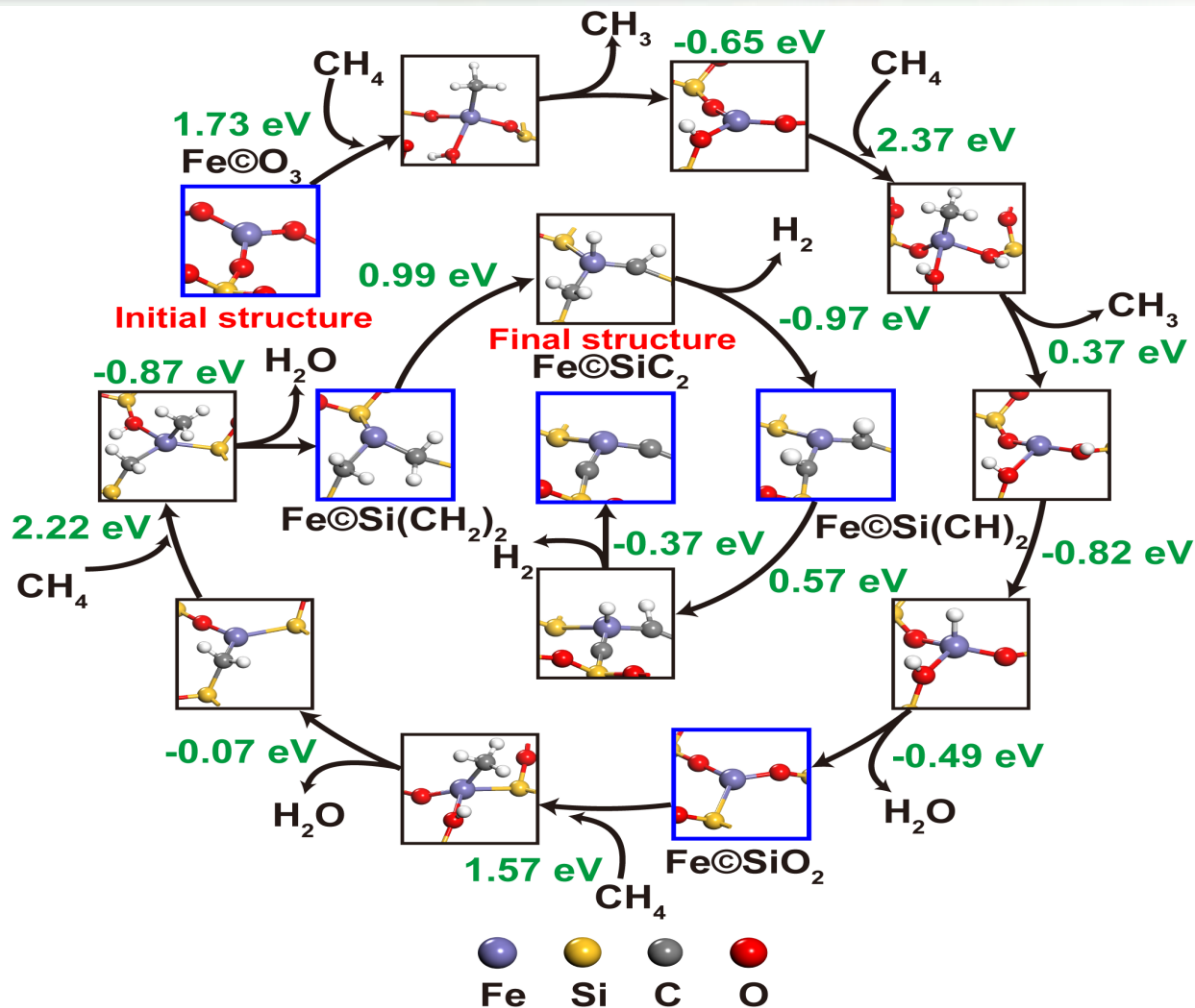
> **During formation of Fe©SiC₂, other active centers (blue) were also found.**

由Fe©O₃产生不同活性中心的自由能 (1200 K)
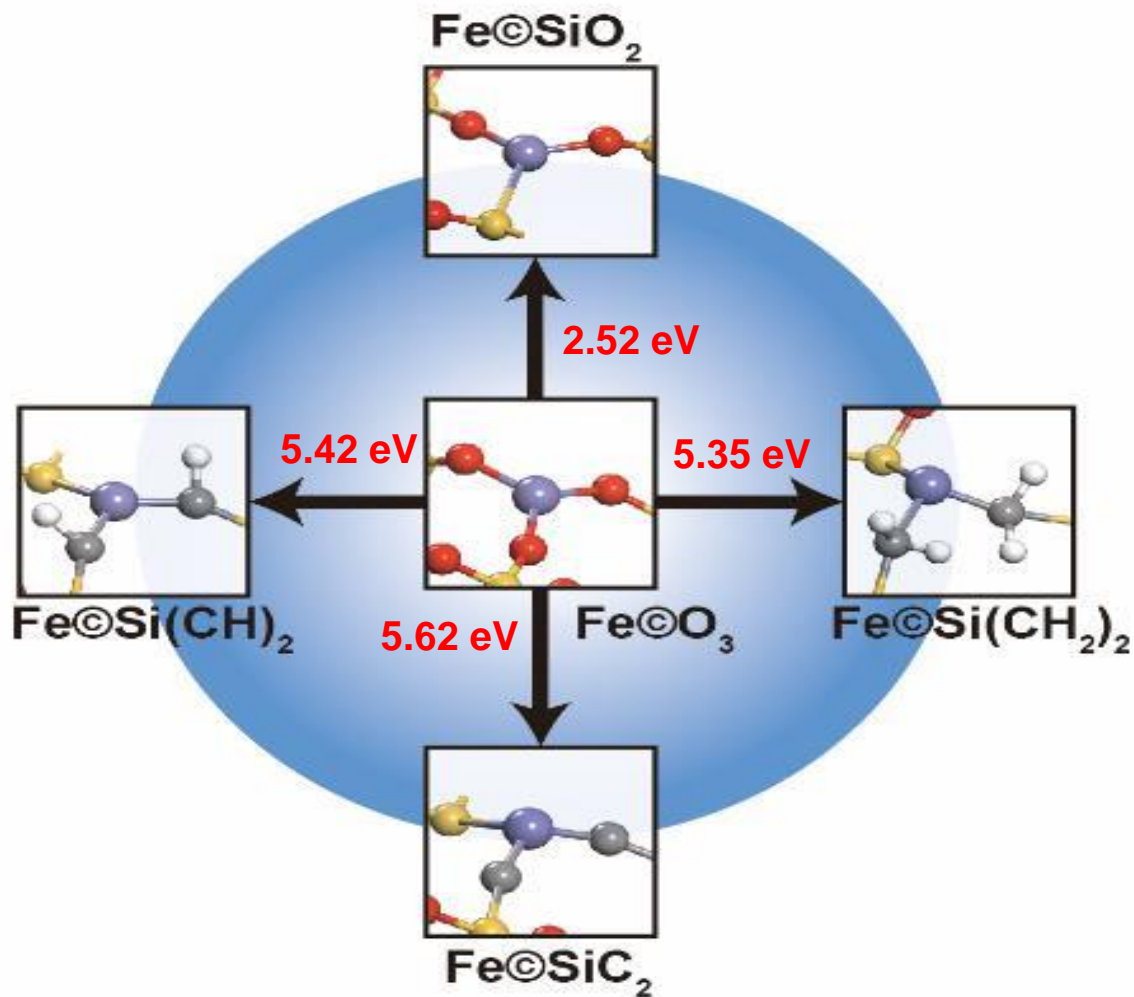
> **O-removal by CH₄-dissociated H is difficult !**

II. 通过甲烷分解产生的CH_x(x=0-3)除氧

Fe©O$_3$

Fe©SiC$_2$

$$CH_4 + 2O^* \rightarrow CH_xO + H_2 + O^* \rightarrow CO + 2H_2 + O^* \rightarrow CO_2 + 2H_2$$
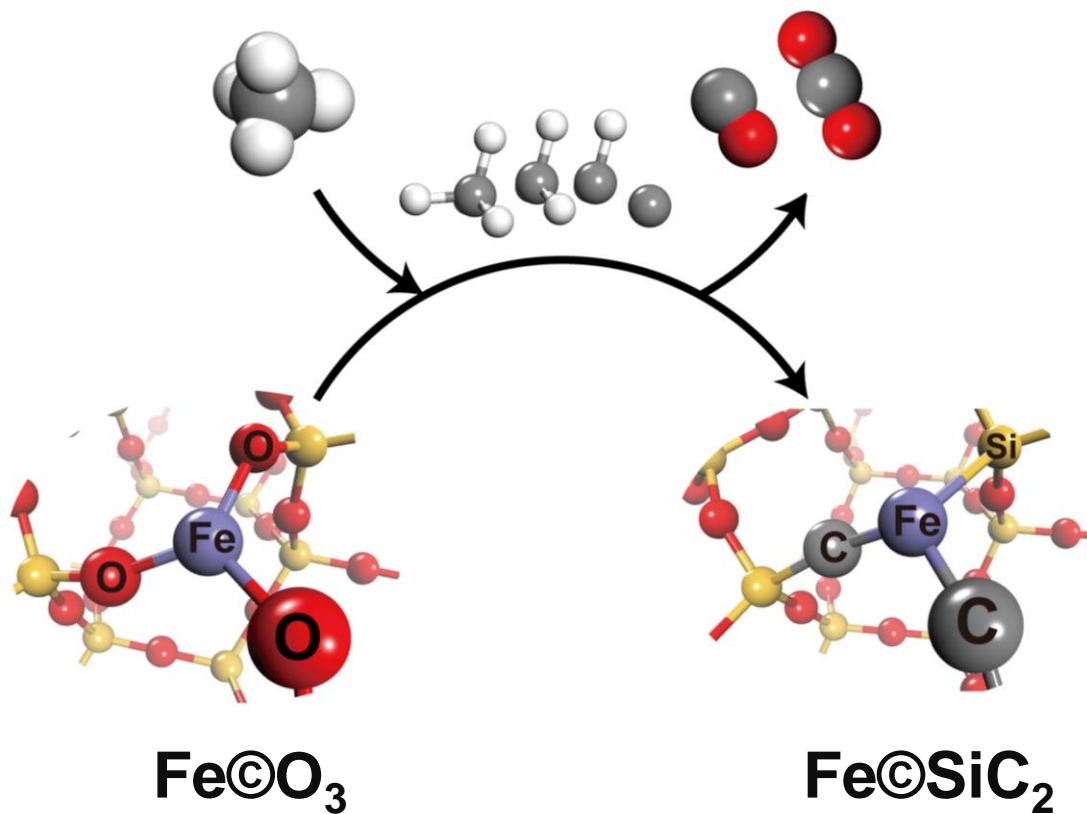
在甲烷分解CHx的作用下 Fe©O$_3$ 到 Fe©SiC$_2$的演变
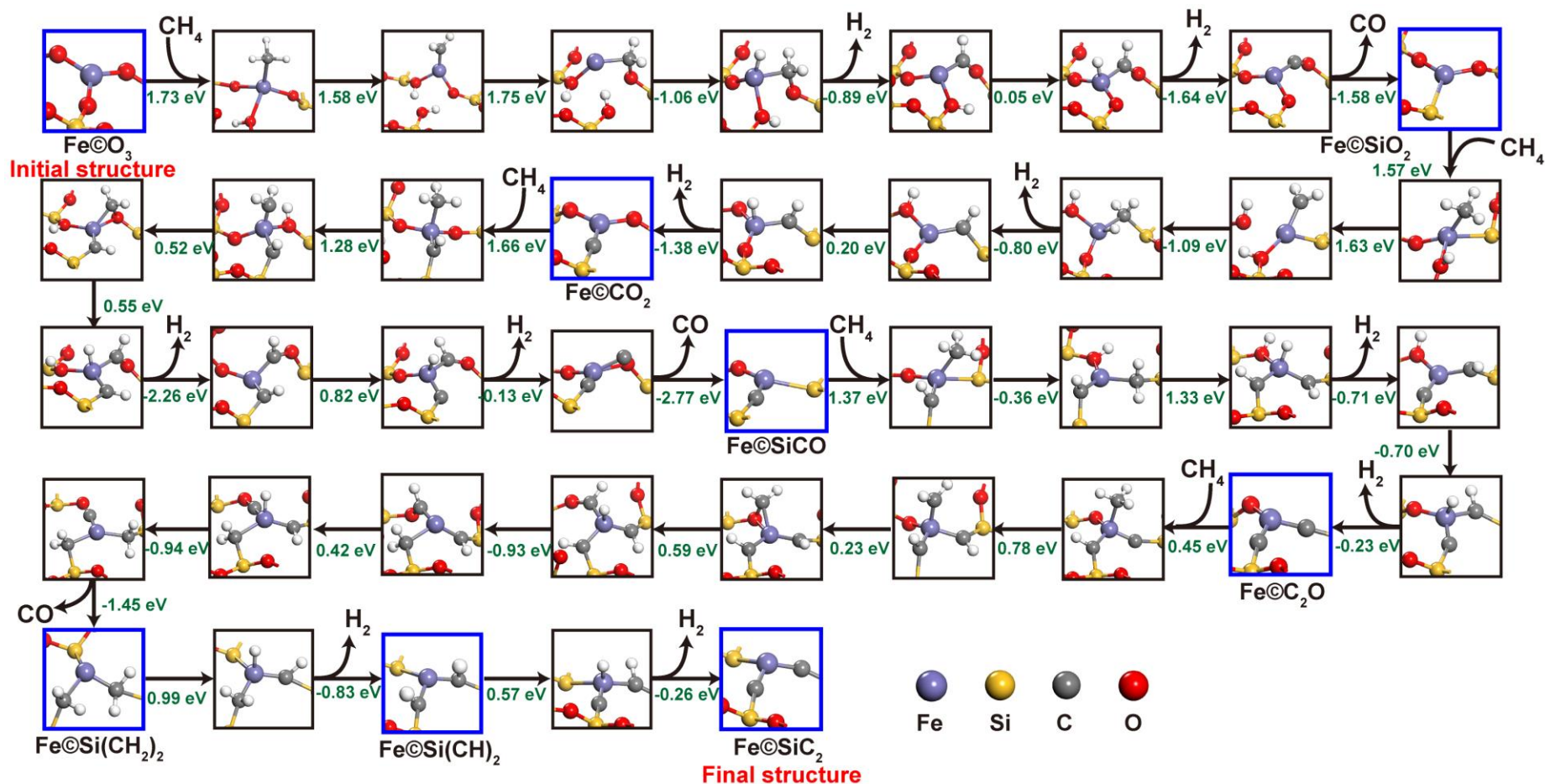
➤ **During formation of Fe©SiC$_2$, other active centers (blue) were also found.**

T.-H. Li, C.-R. Chang, J. Li, et al., J. Phys. Chem. C, 2020, 124, 13656 (front cover).*

由Fe©O₃产生不同活性中心的自由能 (1200 K)

-0.04 eV Fe©SiO₂

-0.41 eV Fe©Si(CH₂)₂

0.08 eV Fe©CO₂

-0.24 eV Fe©Si(CH)₂

-0.26 eV Fe©SiCO

Fe©O₃

0.06 eV Fe©SiC₂

0.43 eV Fe©C₂O
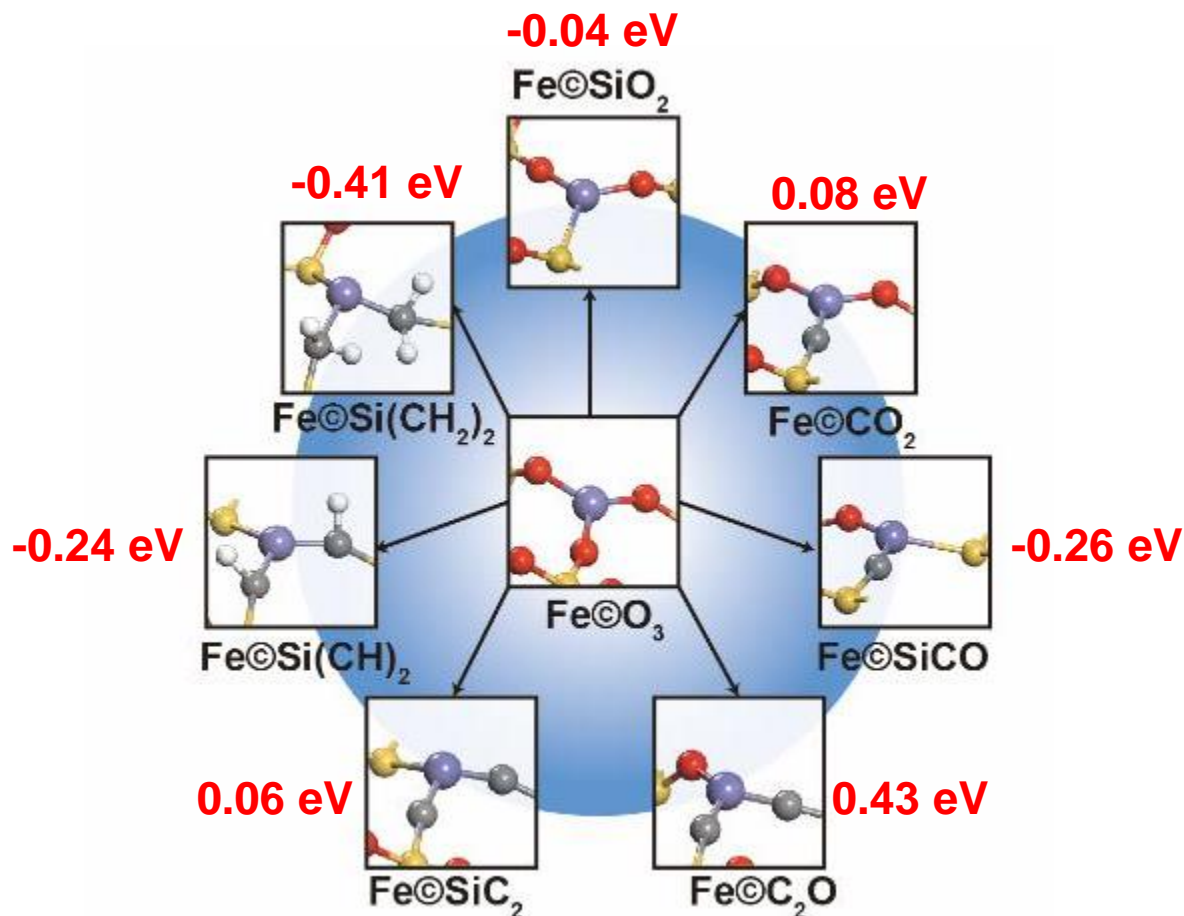
Intrinsic stability of the active sites (CH₂ and CH converting to bare C is facile):
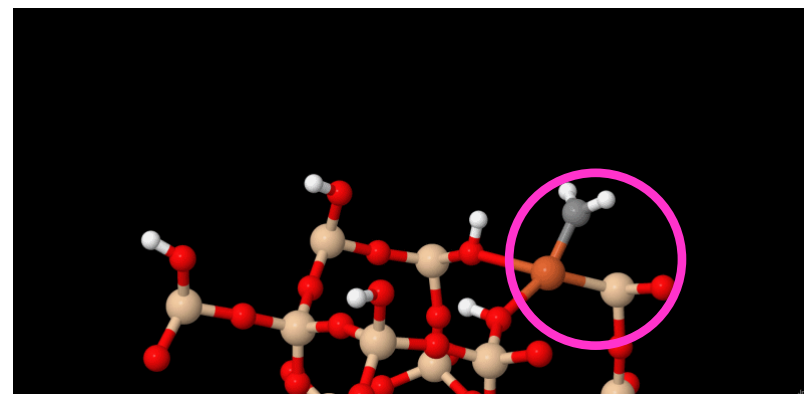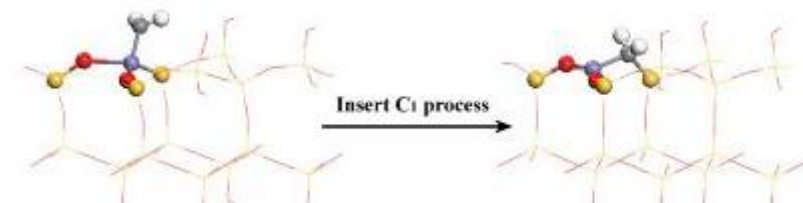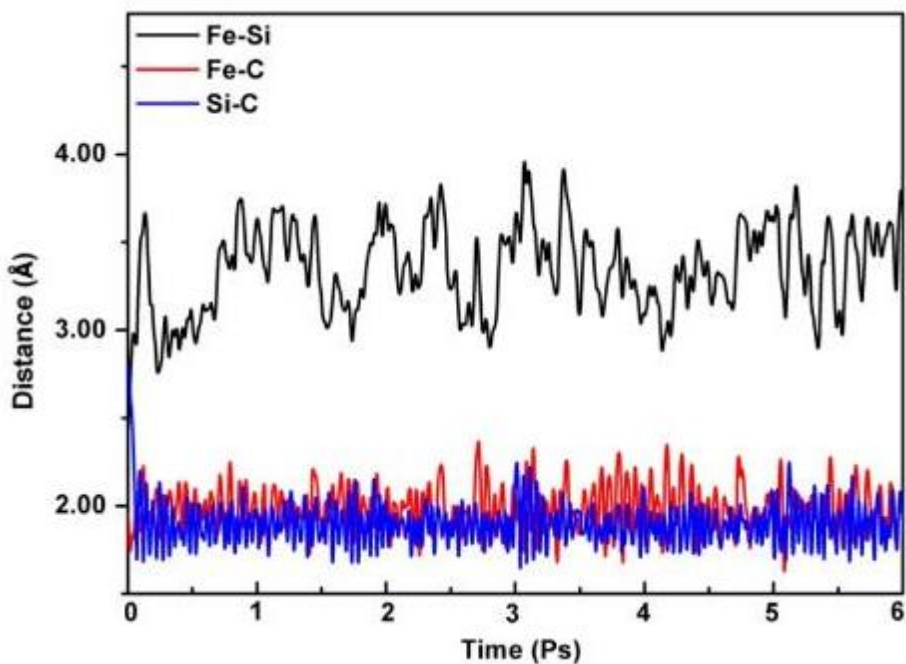
Fe©Si(CH₂)₂ > Fe©SiCO > Fe©Si(CH)₂ > Fe©SiO₂ > Fe©SiC₂ > Fe©CO₂ > Fe©C₂O

AIMD监测到表面氧除走后第一个碳的插入

1363 K，< 1ps

➢ **AIMD simulations support the proposed formation process of Fe©SiC$_2$: O-removal first and CH$_2$ insertion second.**

T.-H. Li, C.-R. Chang, J. Li, et al., J. Phys. Chem. C, 2020, 124, 13656 (front cover).*

第二个碳的插入
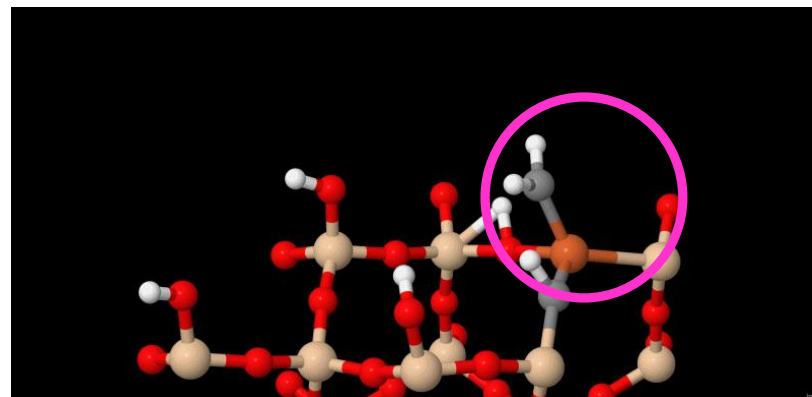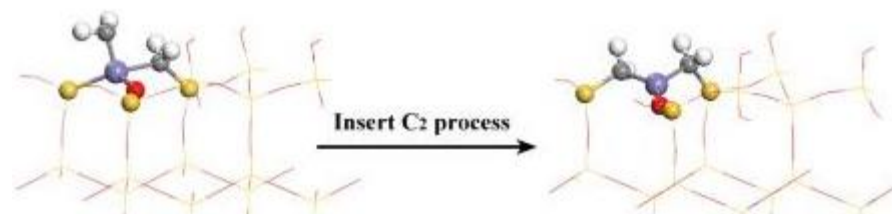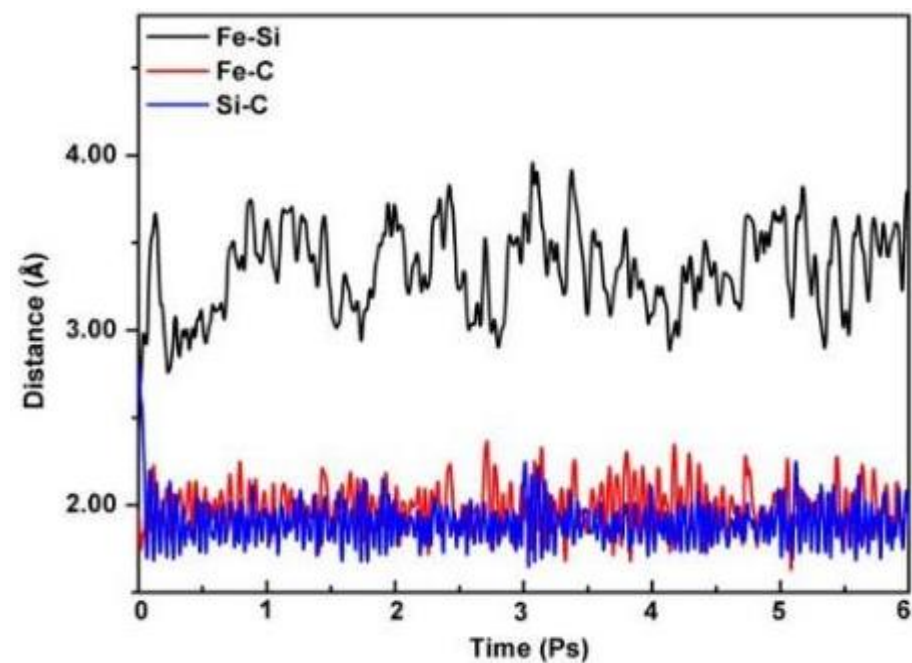
1363 K，< 1ps

- ➢ **AIMD simulations support the proposed formation process of Fe©SiC$_2$: O-removal first and CH$_2$ insertion second.**
- ➢ **Insertion of the 3rd CH$_2$ into O$_{vac}$ becomes unfavorable by ~1 eV.**

T.-H. Li, C.-R. Chang*, J. Li, et al., J. Phys. Chem. C, 2020, 124, 13656 (front cover).

活性中心形成机理小结
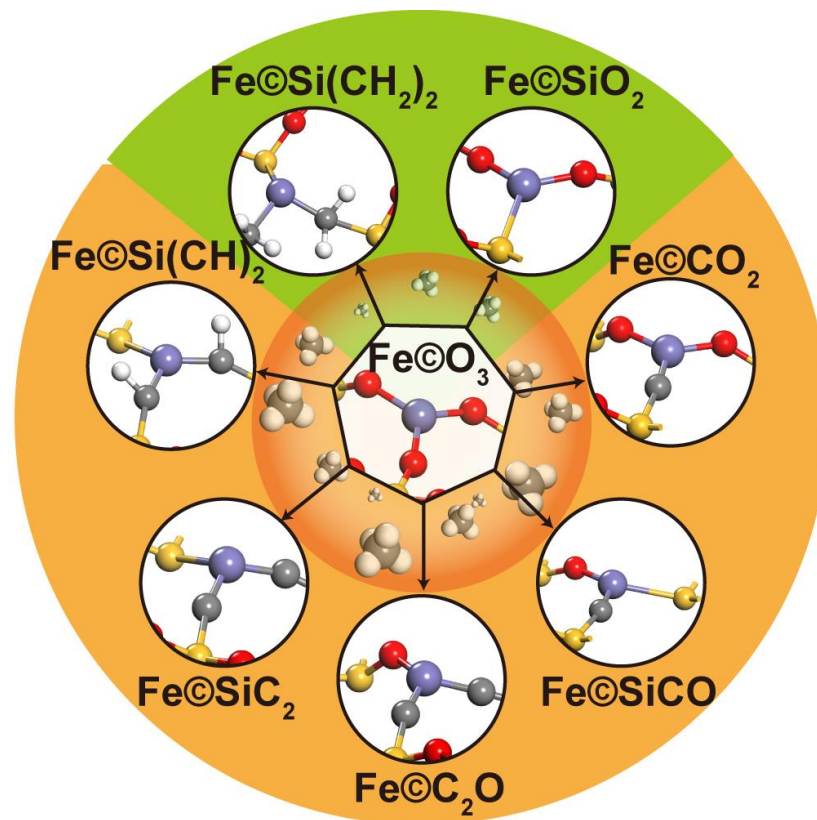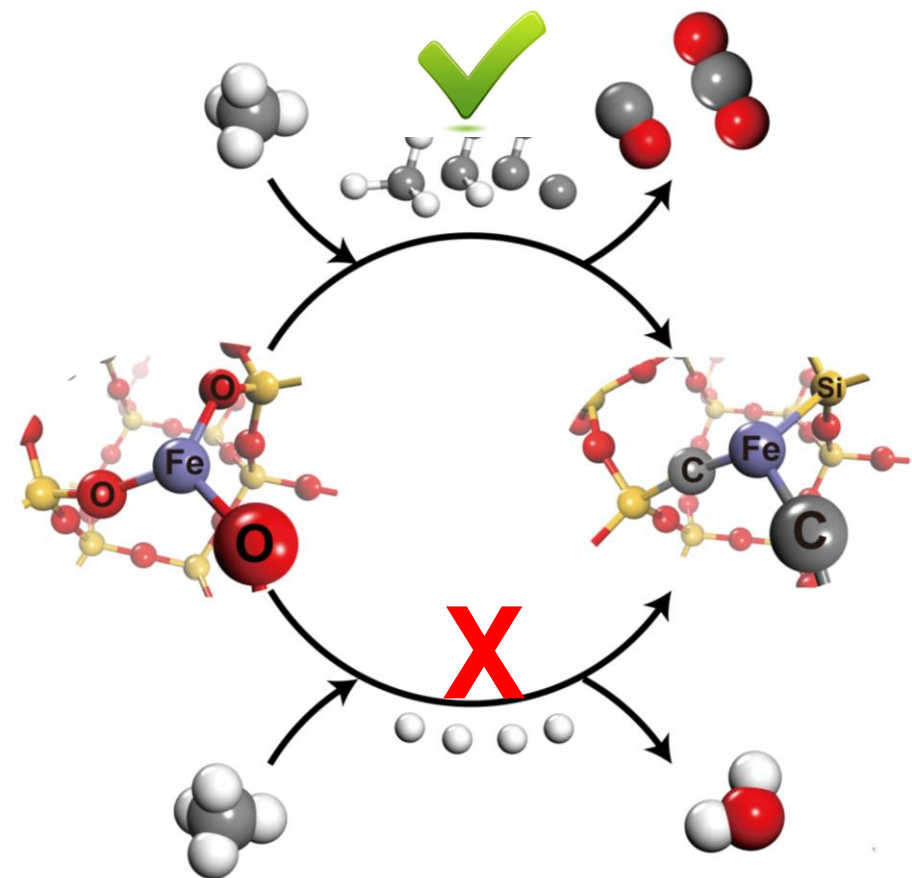
- ➢ **O-removal by CH$_x$ is more favorable than that by H.**
- ➢ **Six other active centers were also found.**
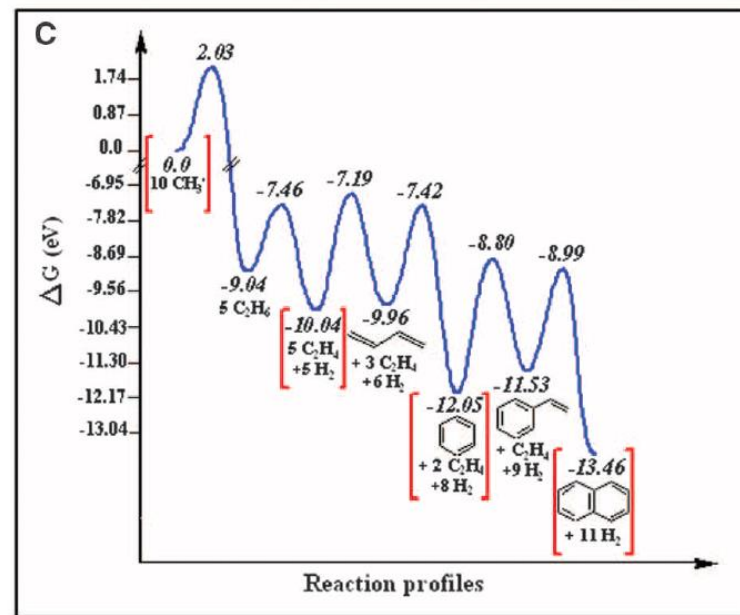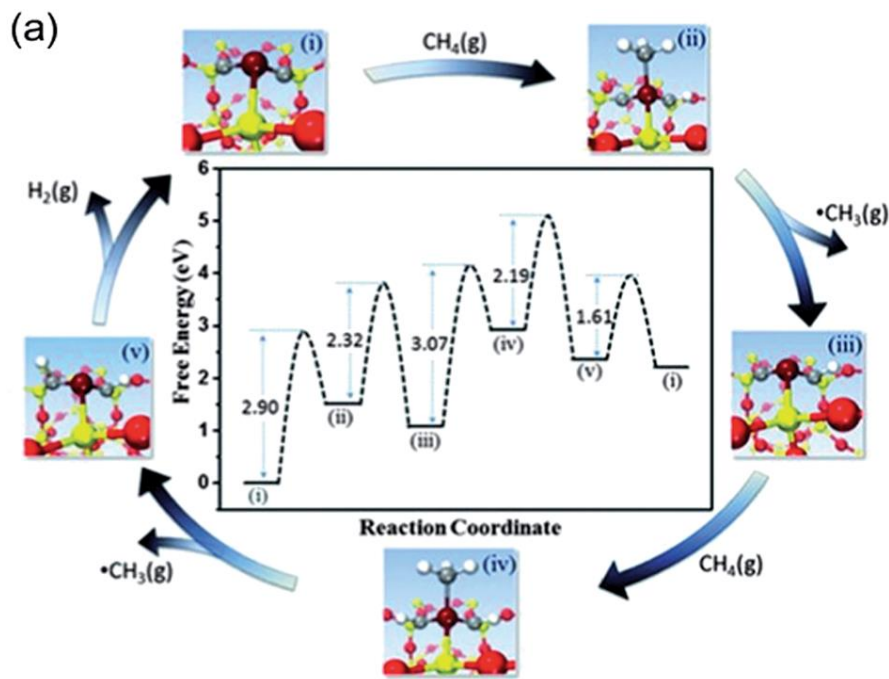
> **The barrier for CH$_3$• desorption is 2.32 eV (estimated, Science 2014).**

> **The selectivity of gas-phase reactions is difficult to control; The barrier to produce C$_2$H$_4$, benzene and nephthalene in the gas phase is up to 3.25 eV.**

X. Guo, X. Bao, et al., Science 2014, 344, 616.*

ReaxFF 反应力场研究气相甲基反应
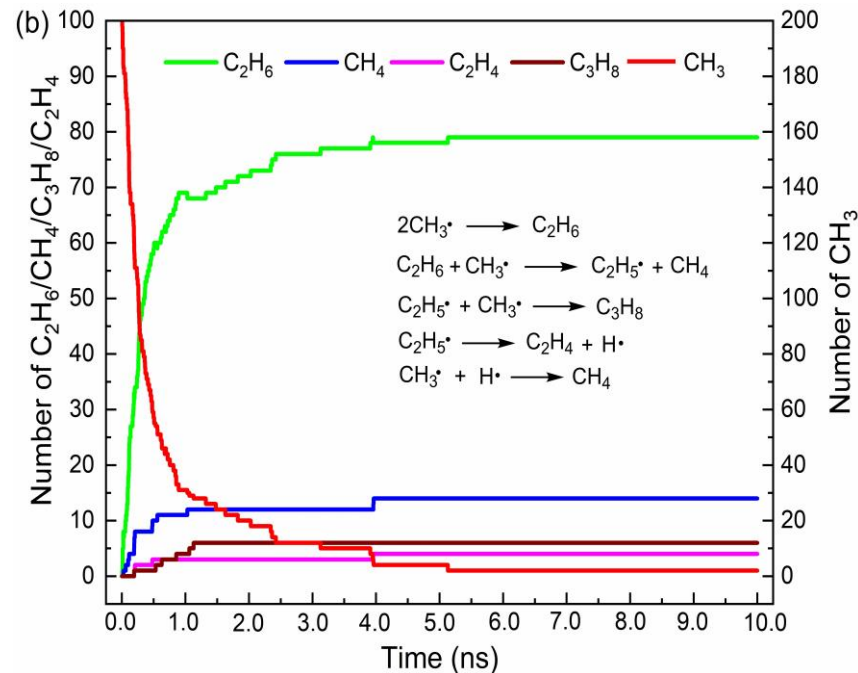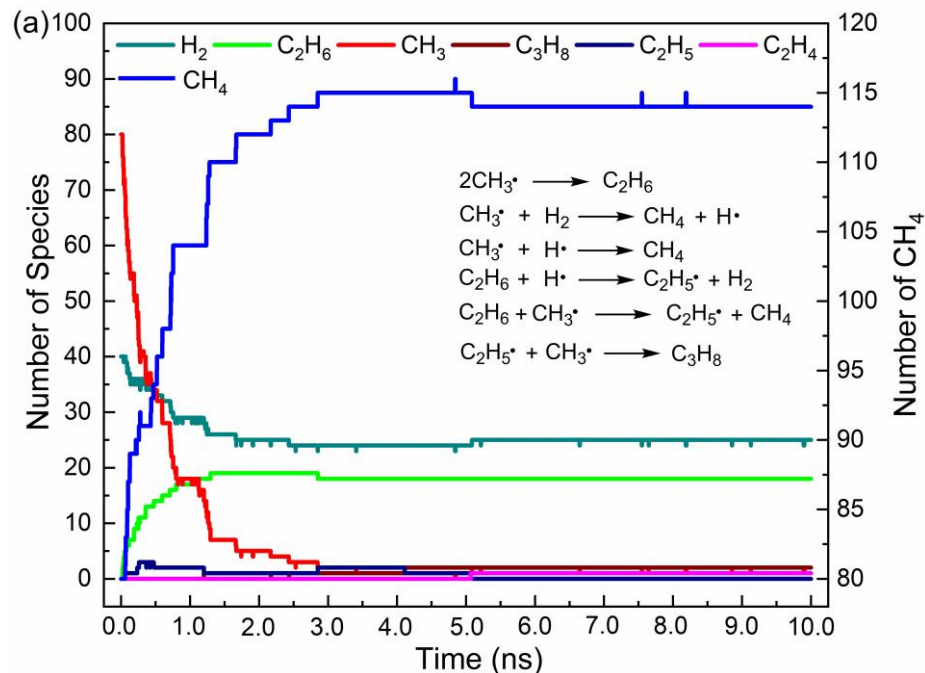
Initial reactant: CH$_4$/CH$_3$•/H$_2$ (80:80:40)
estimated from 50% conversion

Initial reactant: CH$_3$• (200)

➤ **After 10 ns simulation, the main products are C$_2$H$_6$ and CH$_4$ with only 4% C$_2$H$_4$**

➤ **With longer simulation time, C$_2$H$_6$ is hard to convert to C$_2$H$_4$ due to high barrier of > 4.3 eV → $k \approx 10^{-4}$ s^{-1} (difficult to occur)**

Y. Liu, J. Li, C.-R. Chang*, et al., Acta Phys. –Chim. Sin. 2021, 37, 2011012.

H自由基的作用?
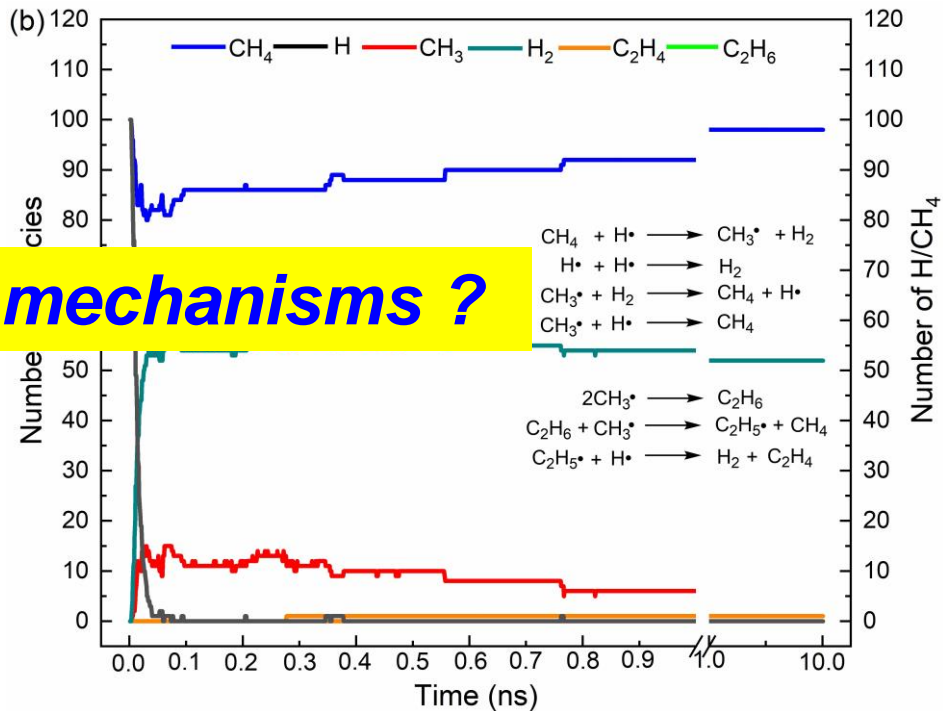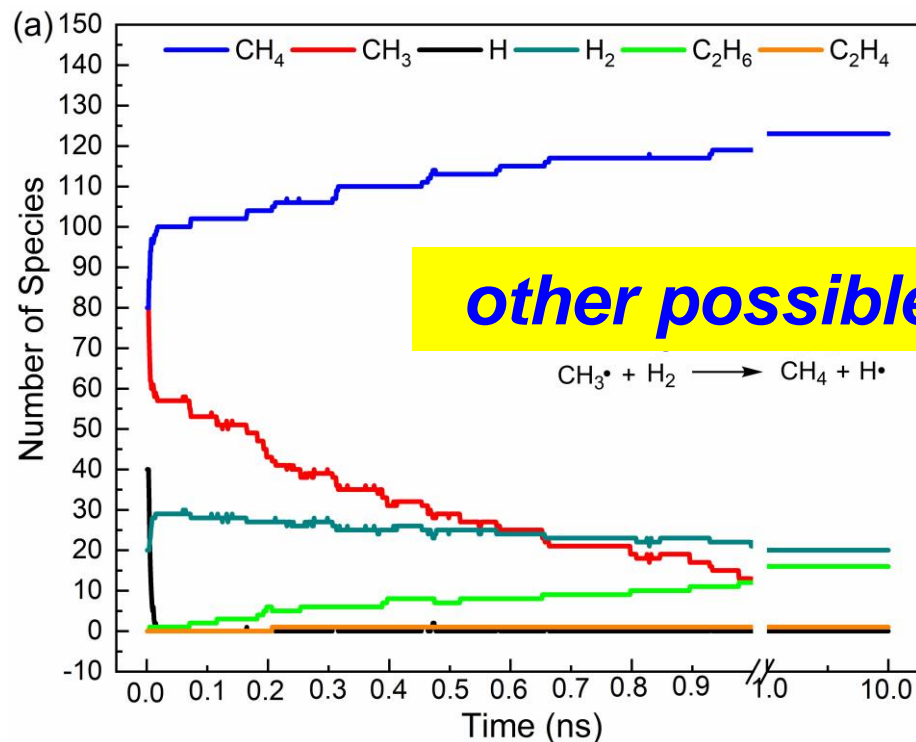
Initial reactant: $CH_4/CH_3•/H_2/H•$ (80:80:20:40) **Initial reactant: $CH_4/H•$ (100:100)**

> **$H•$ like to combine with themselves or $CH_3•$ to form H_2 and CH_4.**

> **The CH_4 activation can be enhanced by $H•$, but the high selectivity of C_2H_4 remains difficult to achieve.**

Y. Liu, J. Li, C.-R. Chang*, et al., Acta Phys. –Chim. Sin. 2021, 37, 2011012.

表面偶联机理？

AIMD observation of CH$_4$ dissociation and CH$_3$ migration

$$CH_4(g) \rightarrow CH_3^* + H^* \qquad CH_3\text{-}Fe \rightarrow CH_3\text{-}C^*$$
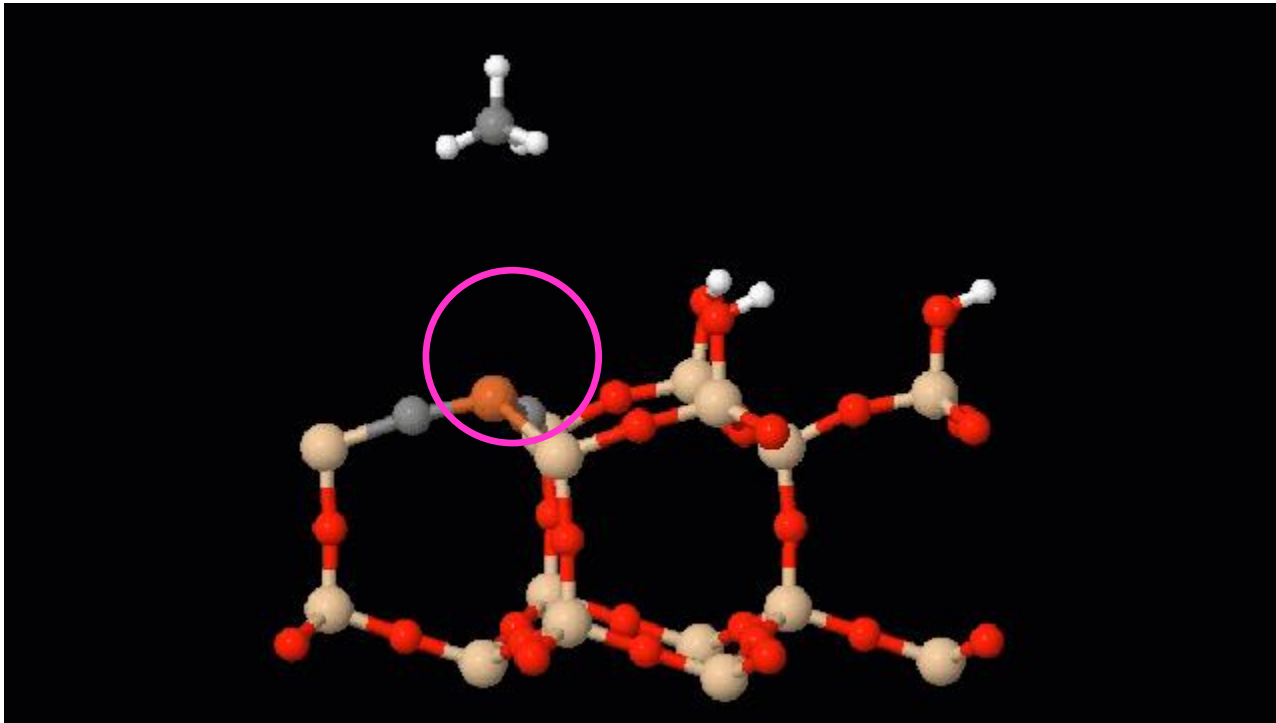
➢ **After methane dissociation, CH$_3$ transfers to C site quickly.**

Y. Liu, C.-R. Chang, J. Li*, et al., Angew. Chem. Int. Ed. 2020, 59, 18586 (VIP)*

100 次AIMD模拟

100 independent AIMD simulations of Fe-CH$_3$
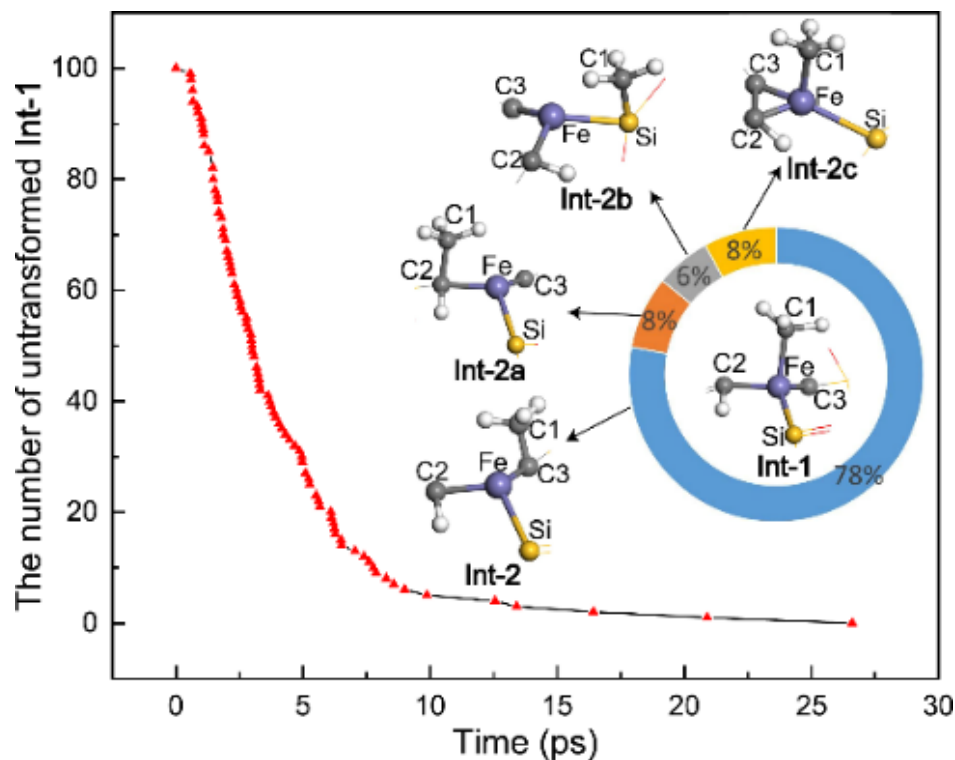
> 78% CH$_3$ transfer to adjacent naked C site, 8% transfer to *CH site, 6% transfer to Si site, 8% remain adsorbed, no CH$_3$* desorption !
> Each AIMD simulation runs ~ 3-26 days on a 24 core supercomputer

Meta-dynamics模拟甲基脱附和转移

Free energy surface of methyl transfer and desorption

$L(C\text{-}C)$ $L(Fe\text{-}C)$
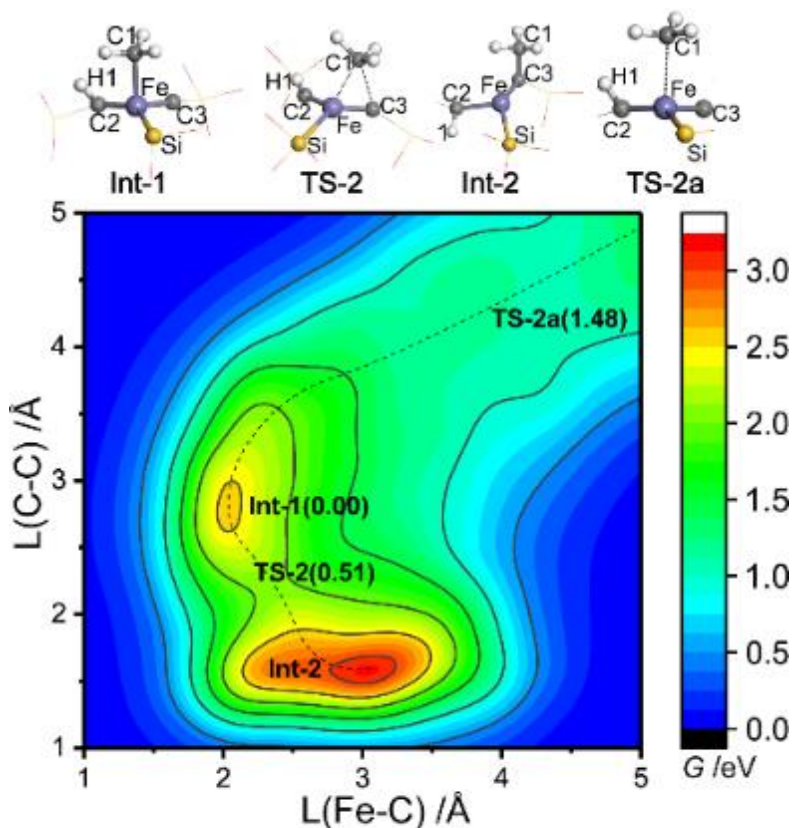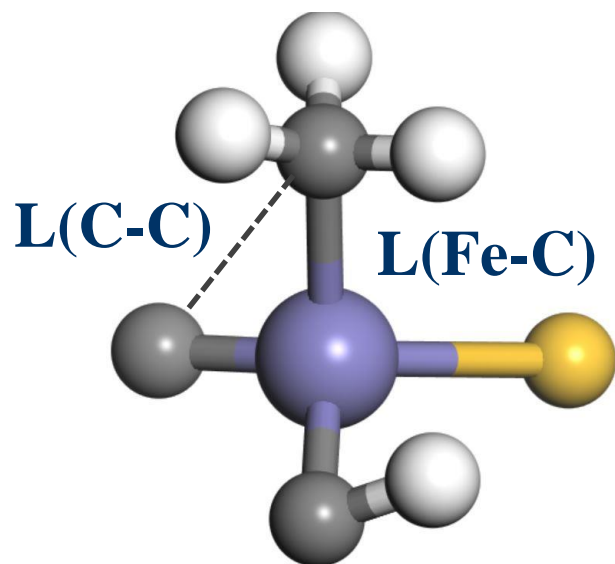
➢ **The free energy barriers of methyl transfer (0.51 eV) and methyl desorption (1.48 eV) at 1363 K indicate the favorable transfer of methyl.**

Y. Liu, C.-R. Chang*, J. Li*, et al., Angew. Chem. Int. Ed. 2020, 59, 18586 (VIP)

甲基转移后的后续转化过程

$CH_3C^* \rightarrow CH_2CH^*$

$CH_3CH^* \rightarrow CH_2CH^* + H^*$
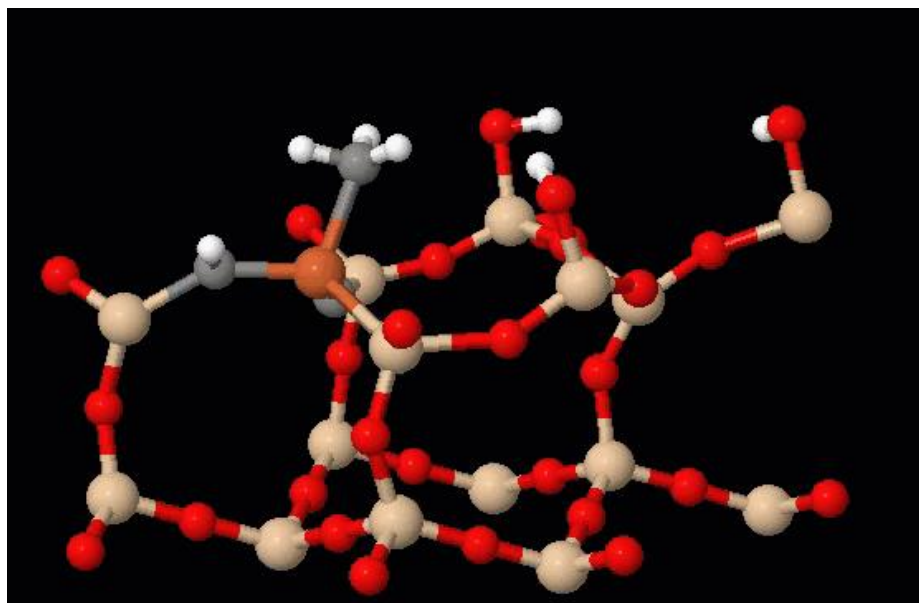
1363 K, < 3.5 ps

1363 K, < 6.7 ps

$CH_2CH^* + H^* \rightarrow C_2H_4^* \rightarrow C_2H_4(g)$
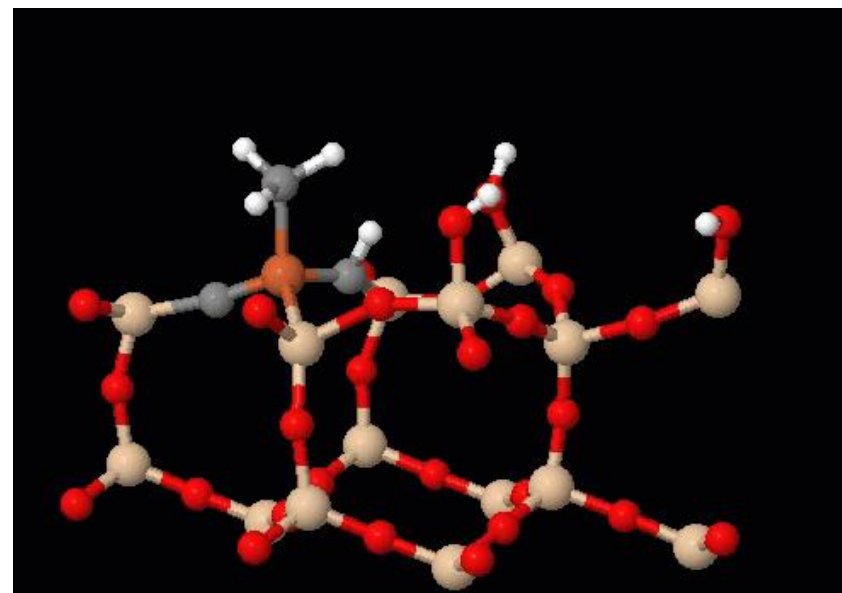
➤ **From both CH_3C^* and CH_3CH^*, a key intermediate CH_2CH^* is formed.**

➤ **Fe site plays a key role in shuttling H to form the final product C_2H_4.**

Y. Liu, C.-R. Chang*, J. Li*, et al., Angew. Chem. Int. Ed. 2020, 59, 18586 (VIP)

甲烷生成乙烯的催化循环
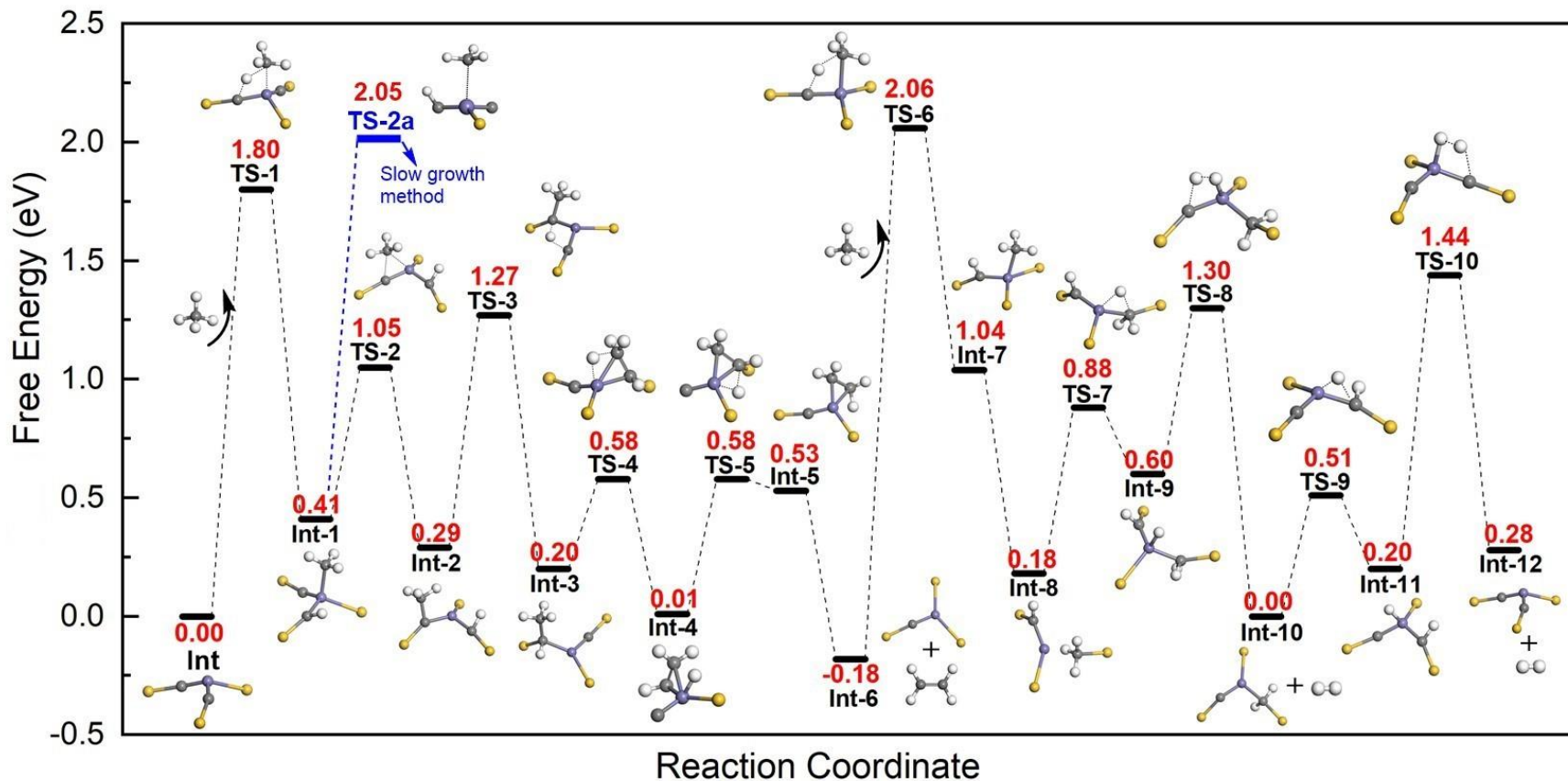
➤ **C$_2$H$_4$ formation (Int-6) on the surface is exothermic by -0.18 eV.**

➤ **The rate-determining step is the 2nd CH$_4$ activation.**

Y. Liu, C.-R. Chang*, J. Li*, et al., Angew. Chem. Int. Ed. 2020, 59, 18586 (VIP)

类-MvK机理的揭示

Quasi-MvK Mechanism
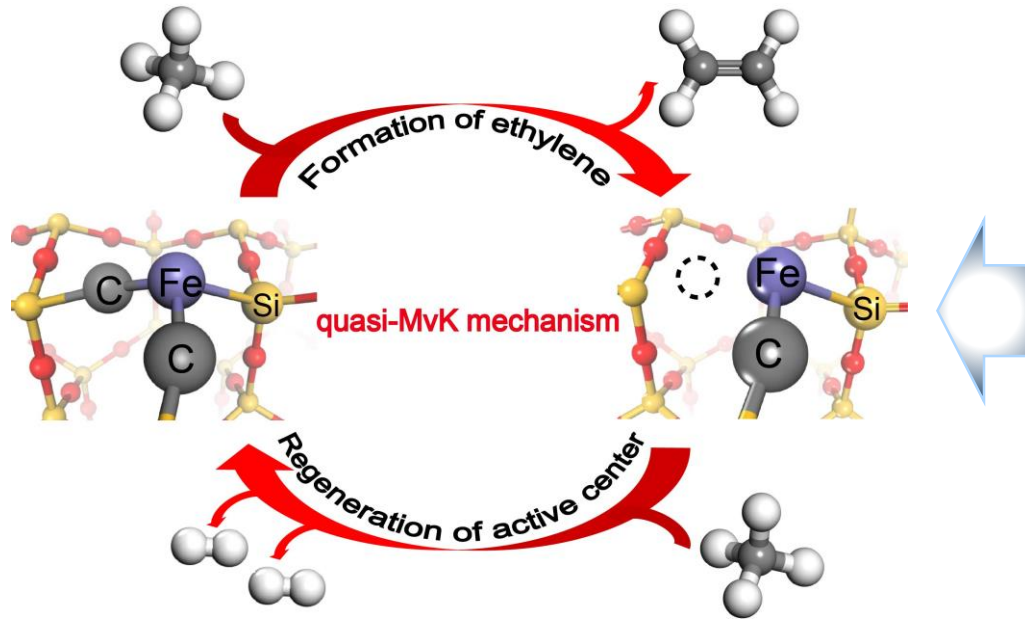
Classical MvK Mechanism
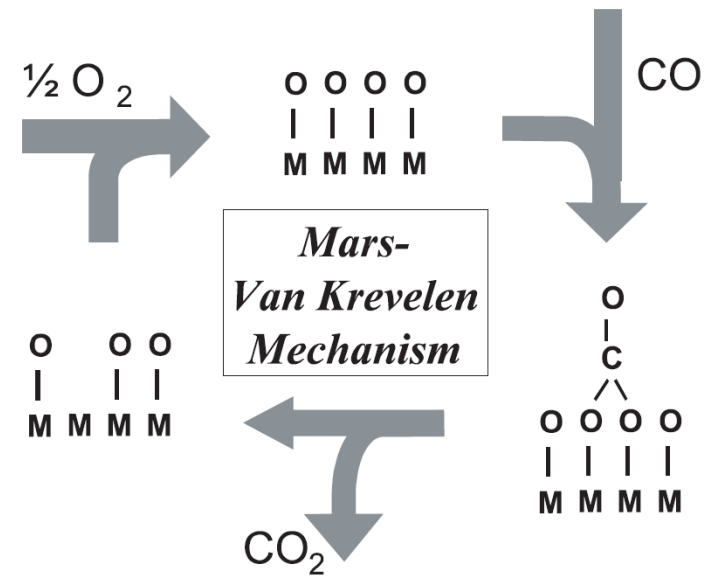
➢ **Ethylene is produced by coupling methane carbon with surface carbon.**

➢ **The active center (Fe©SiC$_2$) is regenerated by another methane's activation.**

实验佐证： FeC_3^- 与甲烷反应生成乙炔

$$FeC_3^- + CH_4 \rightarrow FeC_2H_2^- + C_2H_2$$
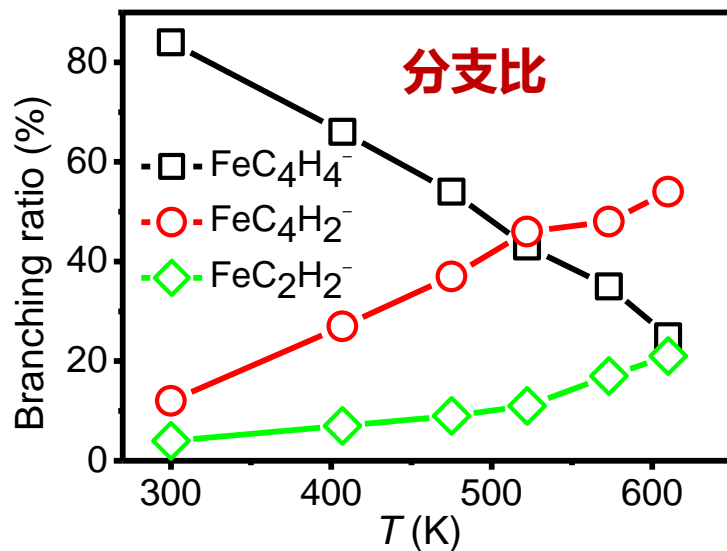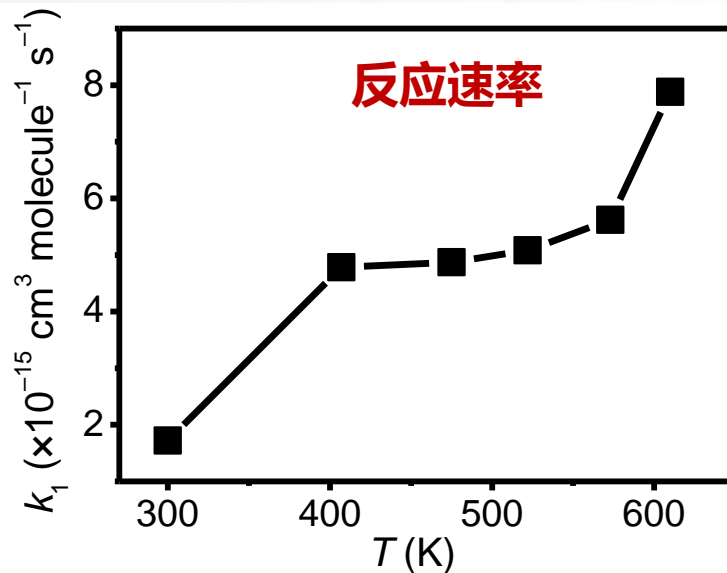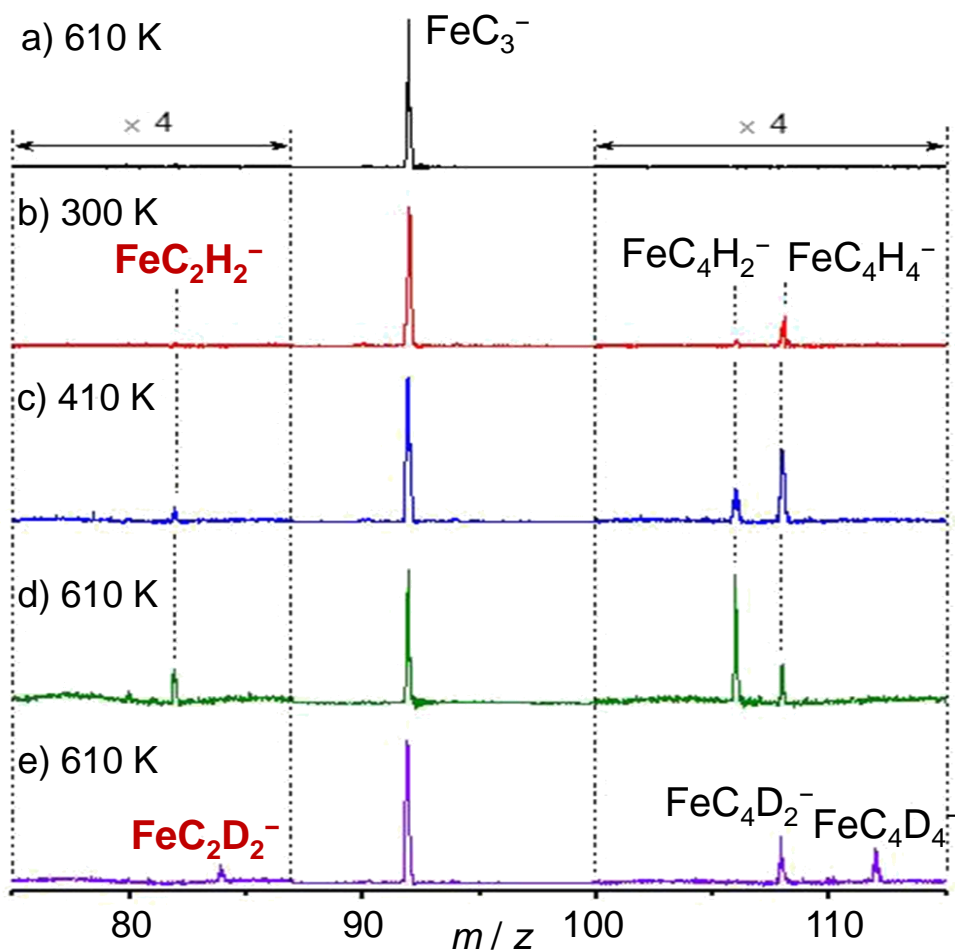
MvK机理的拓展

F-T synthesis on Fe$_5$C$_2$
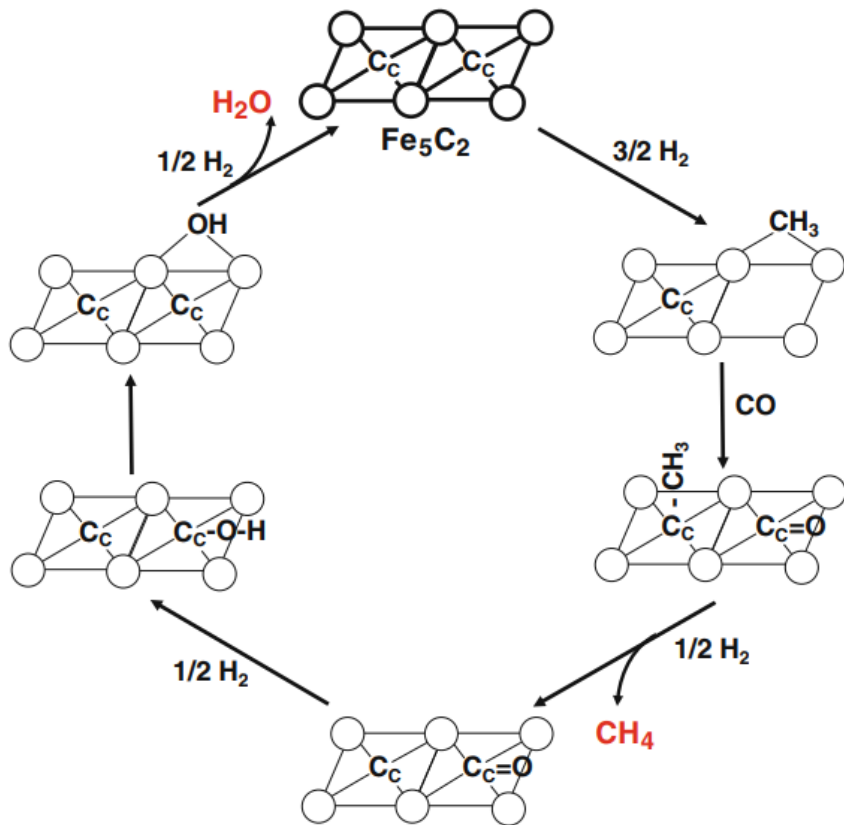
Gracia, et al. Catal. Lett., 2009, 133, 257

Ammonia synthesis on Ni/LaN
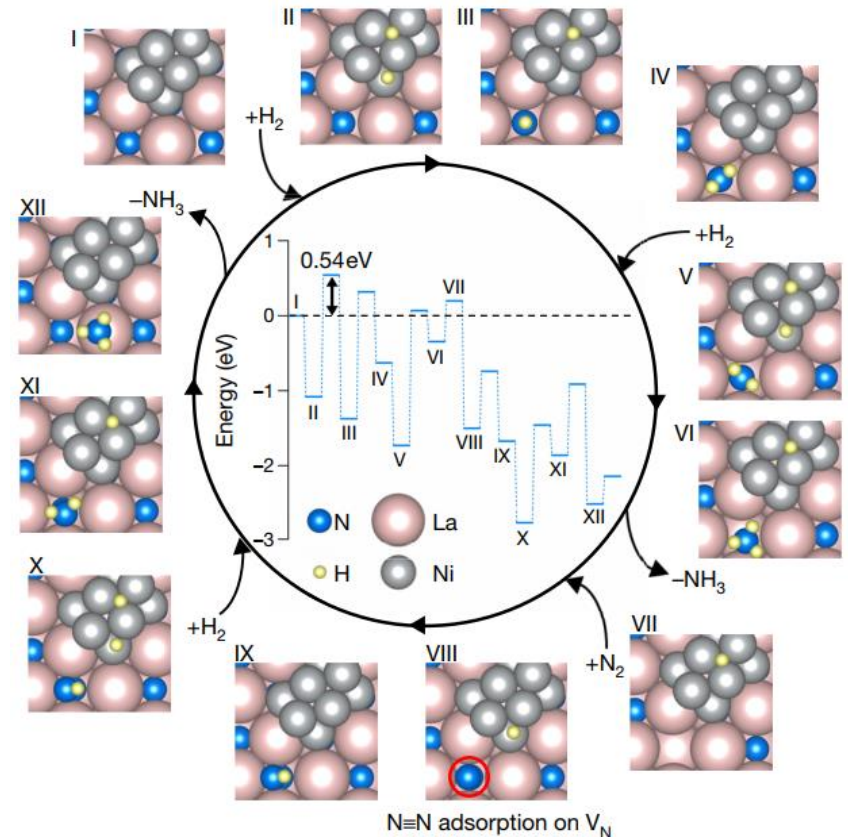
Ye, Kitano, Hosono, et al. *Nature*, 2020, 583, 392

A universal mechanism? metal hydrides, sulfides, phosphides, chlorides, others?

表面反应机理 or 气相反应机理?

Surface Coupling Mechanism
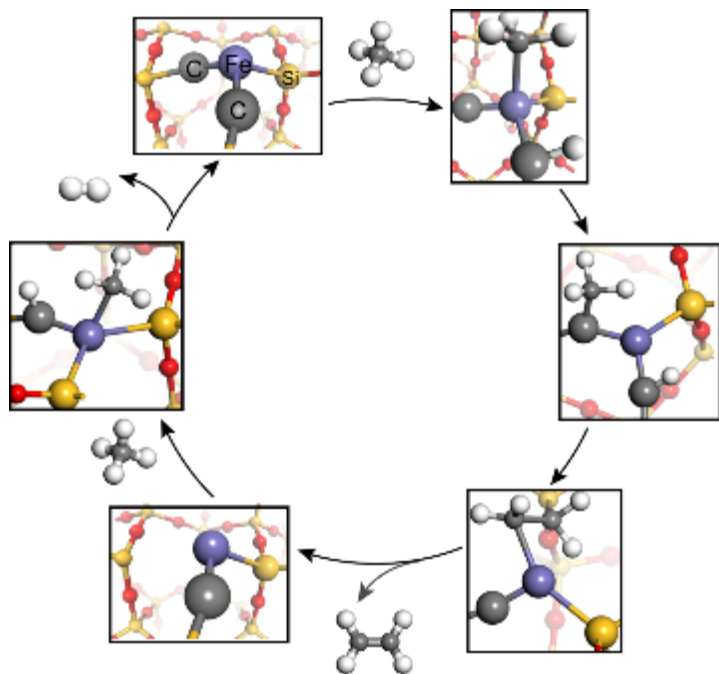
our work

Gas-phase Mechanism
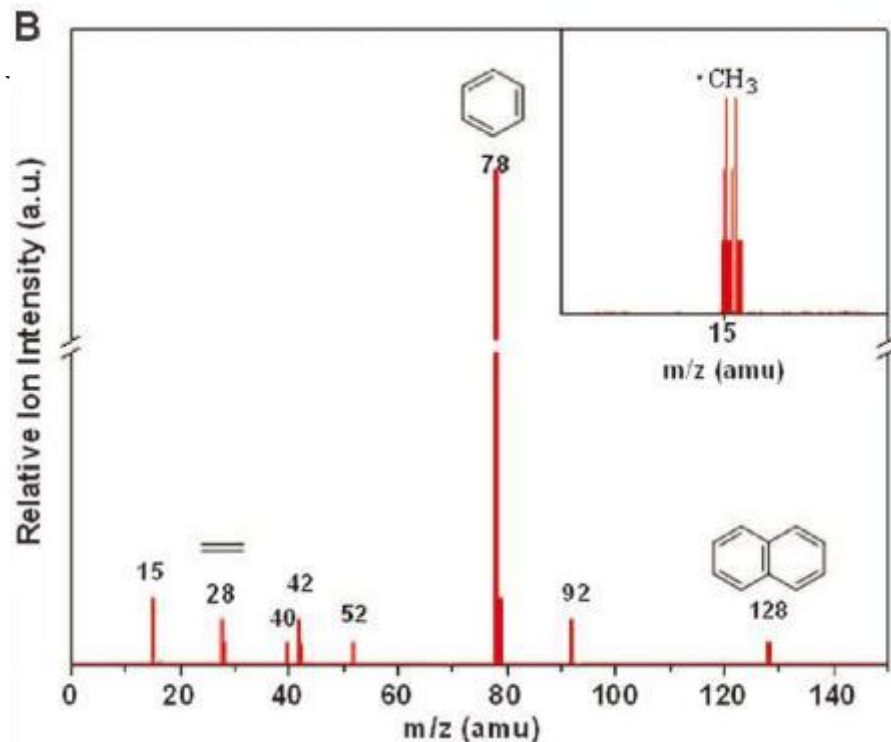
Science, **2014,** *344,* **616**

➢ **Surface coupling mechanism seems contradicted with the experimentally detected gas-phase methyl radical.** *Why ???*

甲烷在其它活性位点的转化

Various active centers
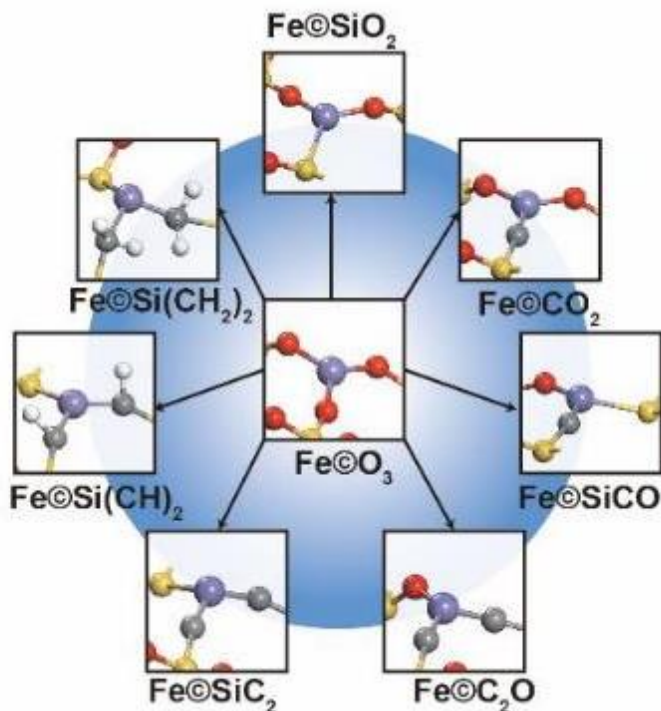
CH$_4$ activation：CH$_4$(g) → CH$_3$*+ H*
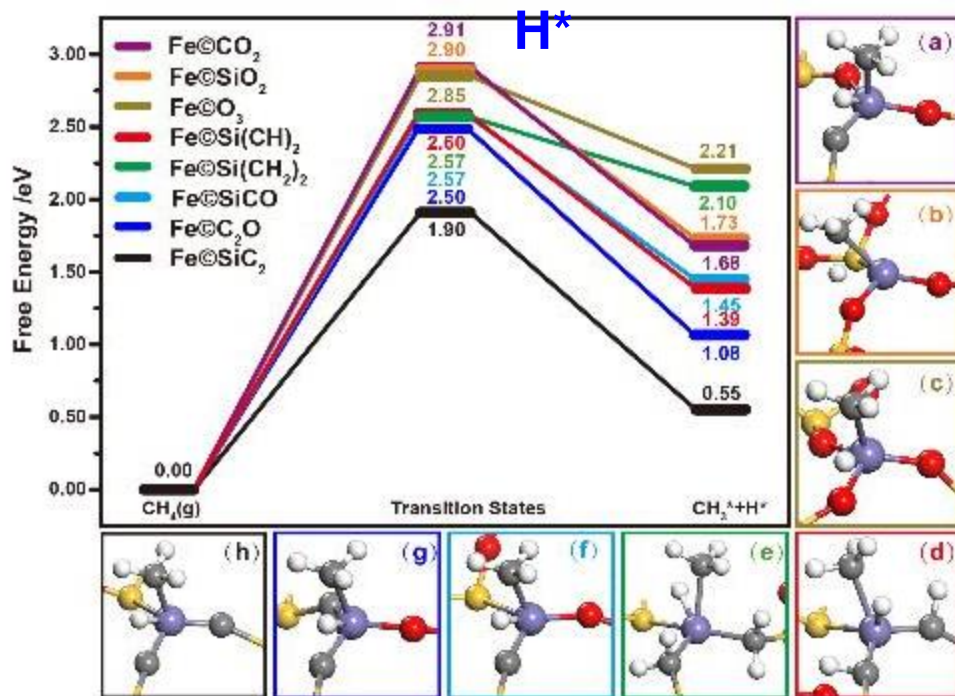
➤ **All the active centers present activity towards methane activation**

Fe©SiC$_2$ > Fe©C$_2$O > Fe©Si(CH)$_2$ > Fe©SiCO > Fe©Si(CH$_2$)$_2$ > Fe©CO$_2$ > Fe©SiO$_2$ > Fe©O$_3$

不同活性中心上甲基的去向

Comparison of CH$_3$* desorption and transfer on different active centers

Active center	Desorption		Transfer	
	$\Delta G_{a\ 1363\ K}$ /eV	$\Delta G_{1363\ K}$ /eV	$\Delta G_{a\ 1363\ K}$ /eV	$\Delta G_{1363\ K}$ /eV
Fe©O$_3$	1.10	-0.63	2.49(O)	2.11
Fe©SiO$_2$	1.57	-0.26	2.44(O)	1.98
Fe©CO$_2$	1.38	-0.80	1.54(O)	0.63
Fe©SiCO	1.50	-0.60	1.94(O)	1.13
Fe©Si(CH$_2$)$_2$	1.46	-0.76	1.51(Si)	0.44
Fe©C$_2$O	1.54	-0.16	0.53(C)	-0.89
Fe©SiC$_2$	1.64	0.14	0.64(C)	-0.12
Fe©Si(CH)$_2$	1.42	-0.83	0.35(C)	-0.83

➢ **Desorption is preferred on O-contained active centers**

➢ **Transfer is preferred on C-contained active centers**

AIMD: 甲基在Fe©O₃上的脱附

$$CH_3^* \rightarrow CH_3\bullet \ (g)$$
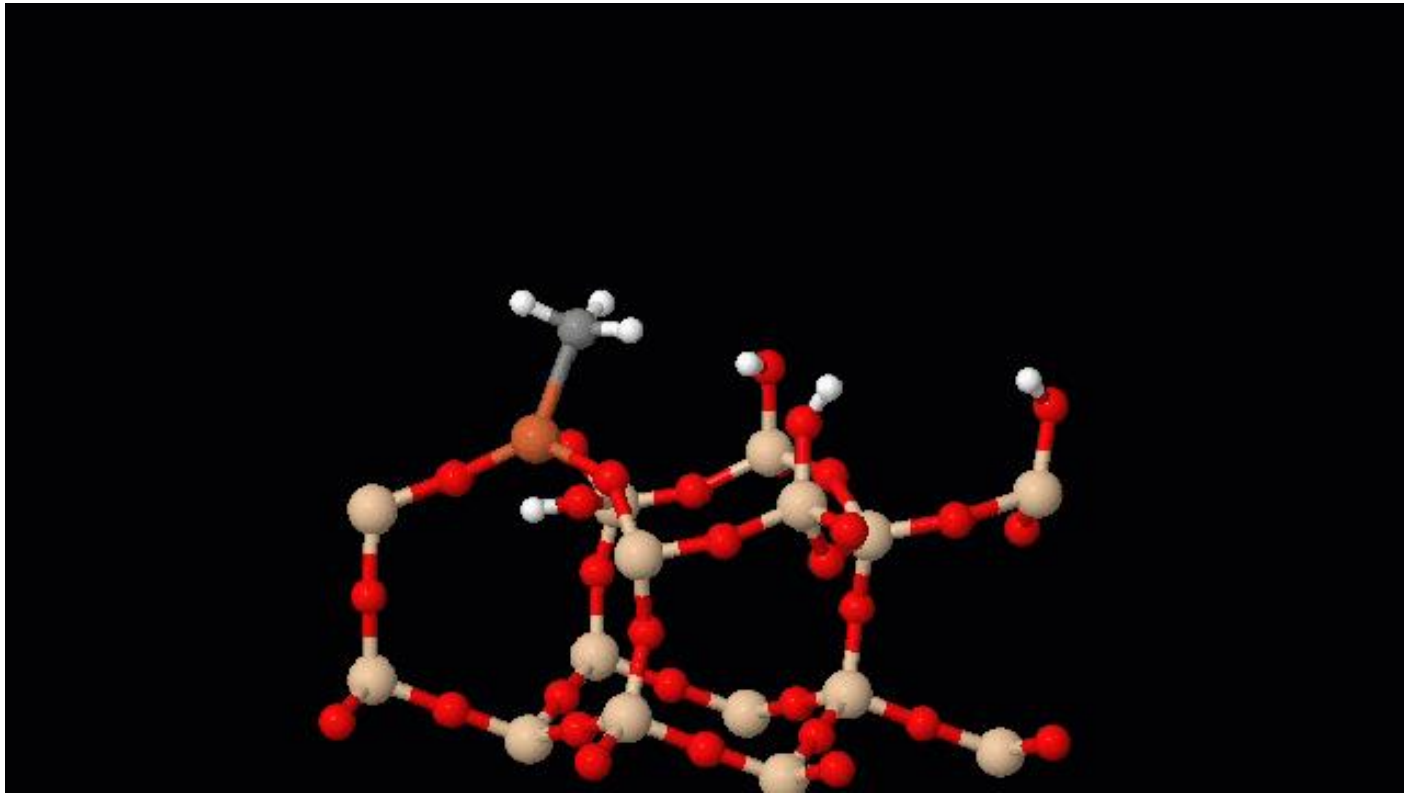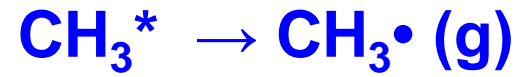
1363K，~ 7.5 ps

动态催化反应机理小结

Combined Gas-phase and Surface Mechanisms!
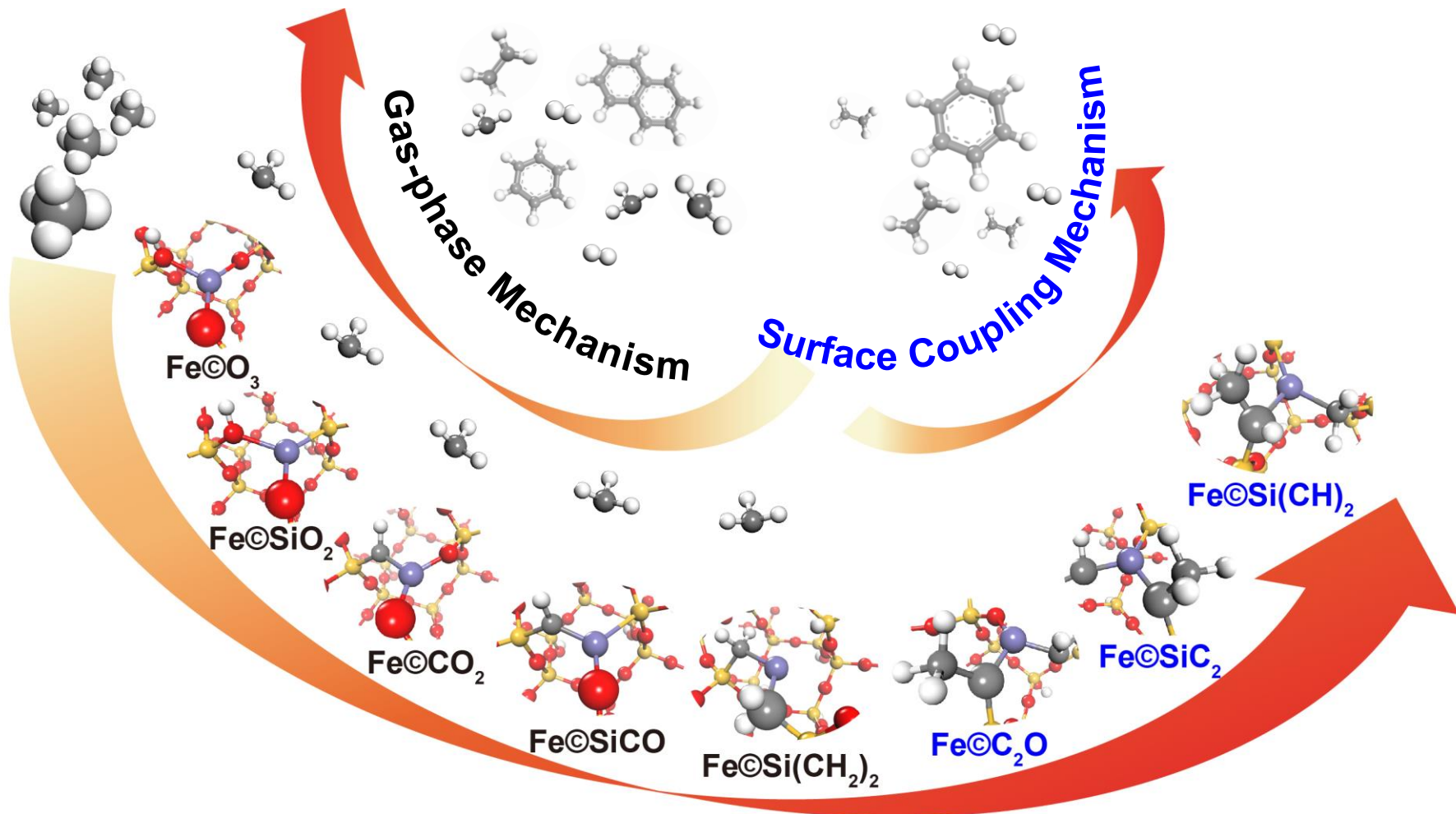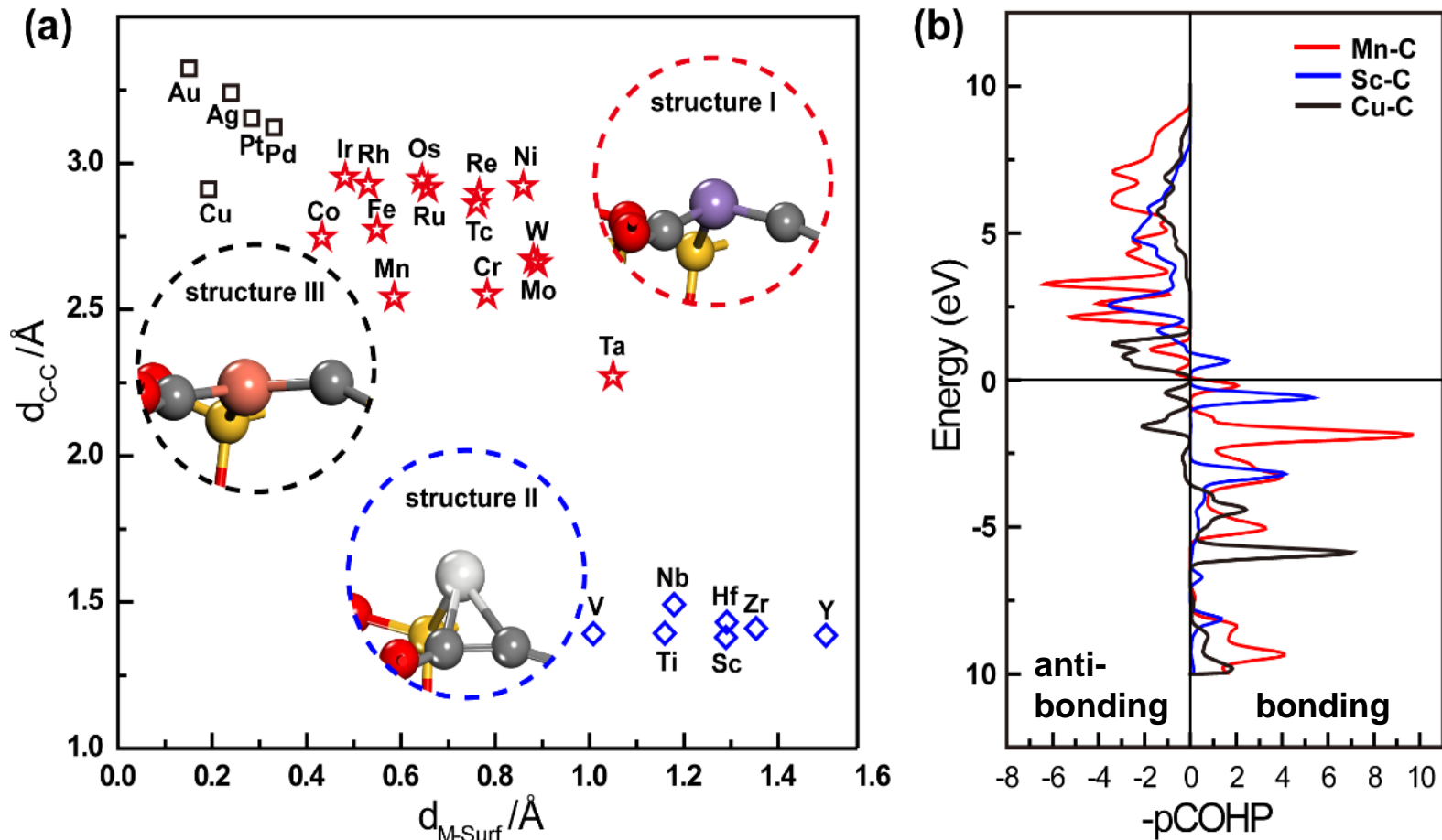
3. 新型单/多中心催化剂的设计
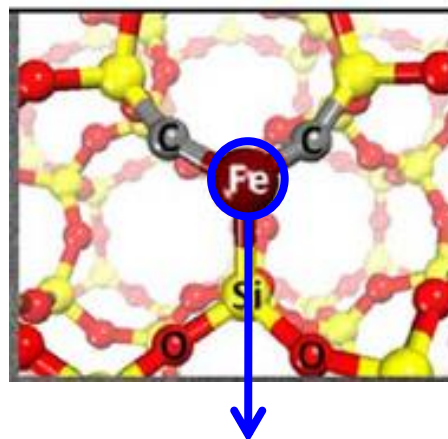
I. 单金属中心催化剂的优化设计

transition metals

通过甲烷吸附能和解离热搜索

> **Mn, Mo, Tc, Ru, Ta, W, Re with strong methane adsorption energy and moderate methane dissociation energy are selected.**
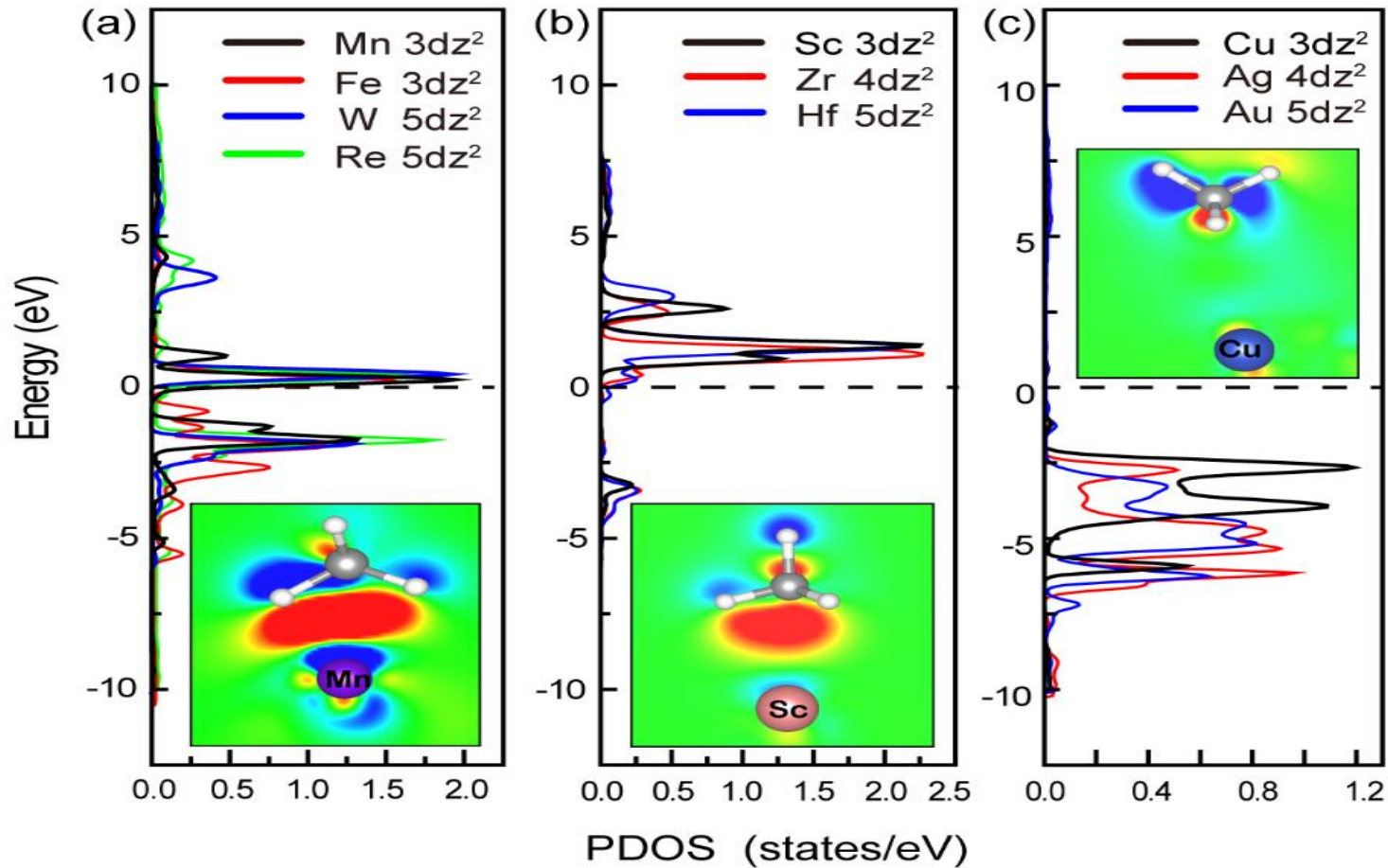
S.-Y. He, J. Li, C.-R. Chang*, et al., J. Chem. Phys. 2021, 154, 174706.

$$CH_4(g) \rightarrow CH_4^* \rightarrow CH_3^* + H^*$$

Metal	E_{ads}/eV	E_a/eV	$\Delta E/eV$
Tc	-0.46	0.62	-1.34
Mo	-0.47	0.58	-0.57
Ta	-0.39	0.50	-0.90
Fe	-0.38	0.46	-0.85
W	-0.50	0.30	-1.02
Re	-0.51	0.22	-1.68
Mn	-0.34	0.14	-1.18
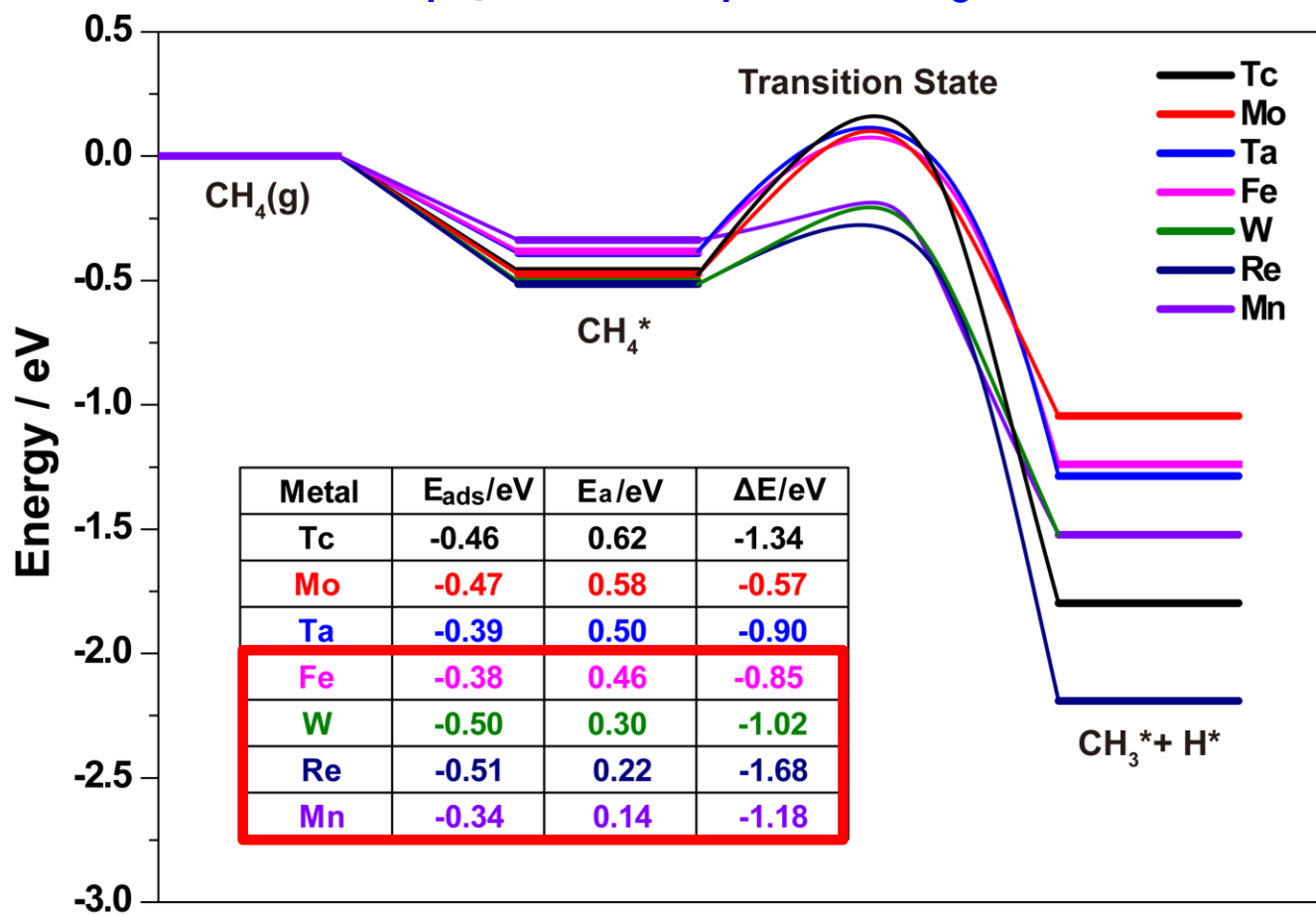
➢ **Fe, W, Re, Mn show low activation barrier for CH$_4$ dissociation.**
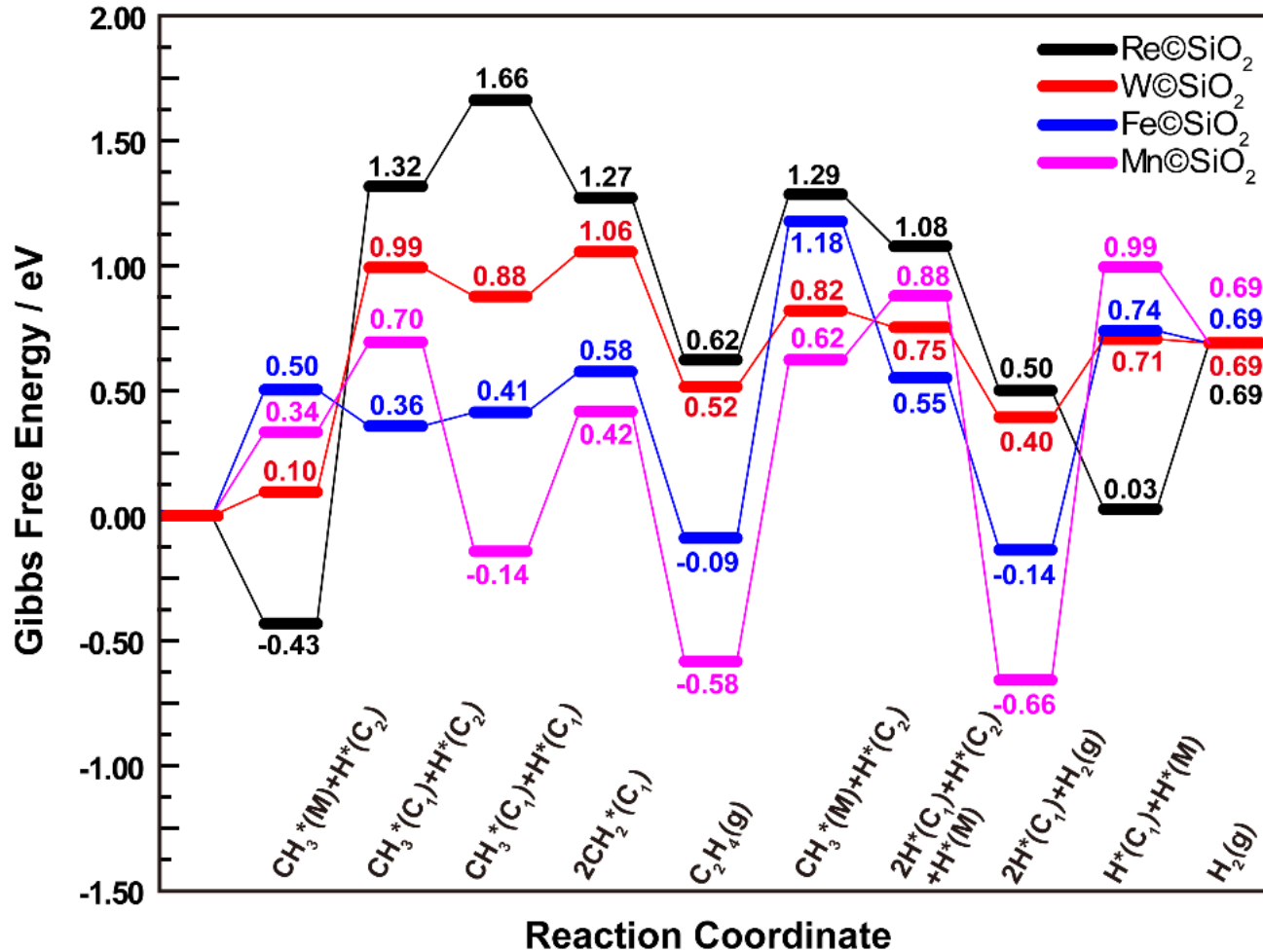
优异催化性能的原因分析

- Fe, W, Re, Mn are well supported on the surface.
- The bonding orbitals are all below the Fermi level and the antibonding orbitals are all above the Fermi level

优异催化性能的原因分析

> **the dz² orbitals of the four cross over the Fermi level, which could lead to the significant activation of methane.**

目标催化剂上的催化反应循环

> **W©SiC$_2$ exhibits the best performance !**

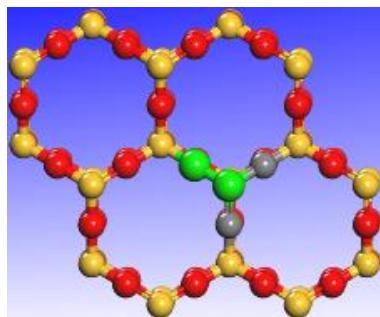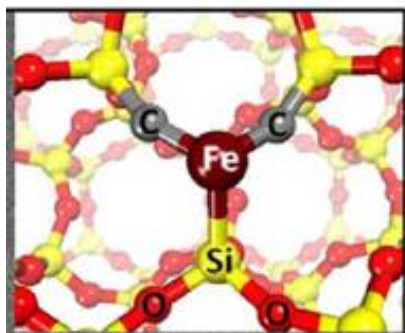*S.-Y. He, J. Li, C.-R. Chang*, et al., J. Chem. Phys. 2021, 154, 174706.*

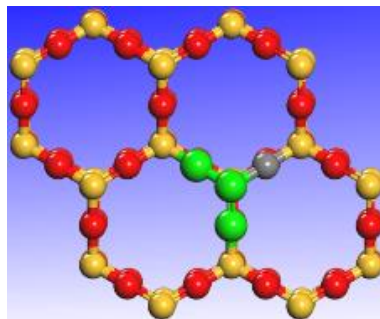# 单原子位点存在的问题

- **Unfavorable C-C coupling**

  (both gas-phase and quasi MvK mechanisms are not easy)
- **Difficult selectivity control**

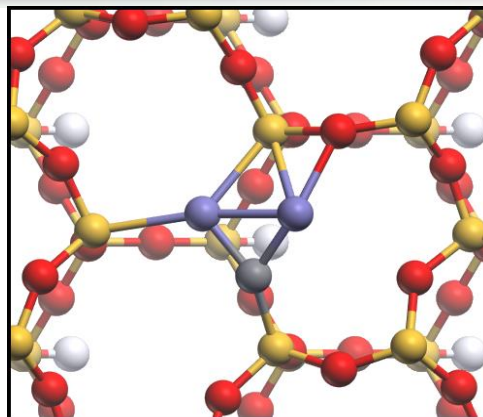 **(40-50% ethylene, 50-60% benzene and naphthalene)**

Dual Active Sites

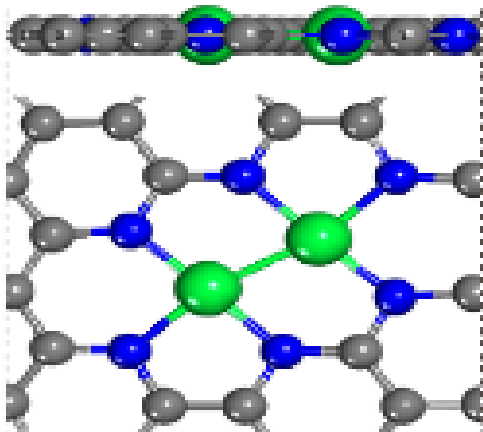**Tri-Active Sites**

Objective:
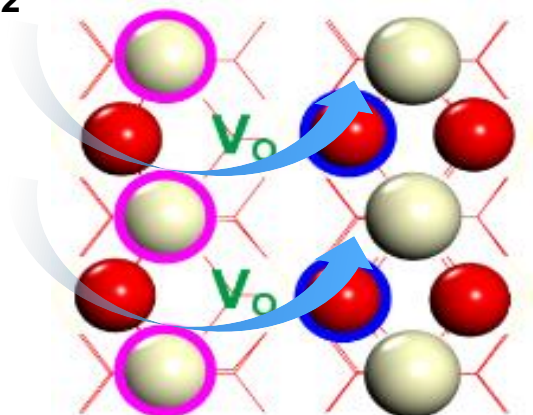
Enhance C-C coupling

Improve C2 selectivity

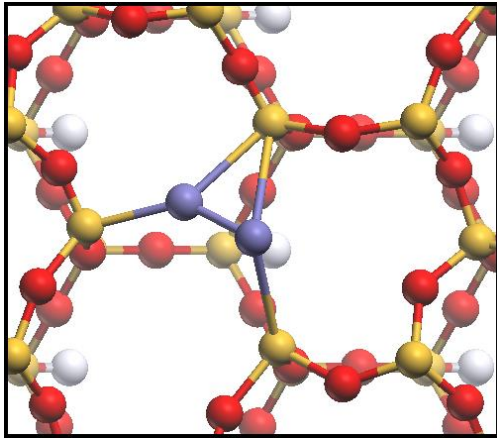**Prevent coking**

II. 双活性位催化剂设计
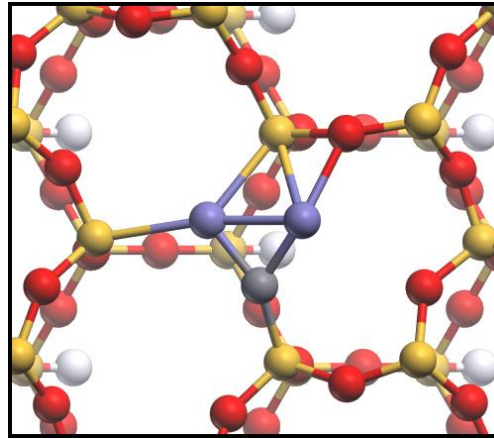

Fe$_2$C©SiO$_2$

Co$_2$-N-C

FLPs-CeO$_2$

J. Wang, C.-R. Chang, Y. Wu*, et al., J. Am. Chem. Soc. 2017, 139, 17281;*
S. Zhang, Z.-Q. Huang, C.-R. Chang, Y. Qu*, et al., Nat. Commn. , 2017, 8, 15266;*
Z.-Q. Huang, C.-R. Chang, J. Li, ACS Catal., 2019, 9, 5523; 2021, 11, 13149.*
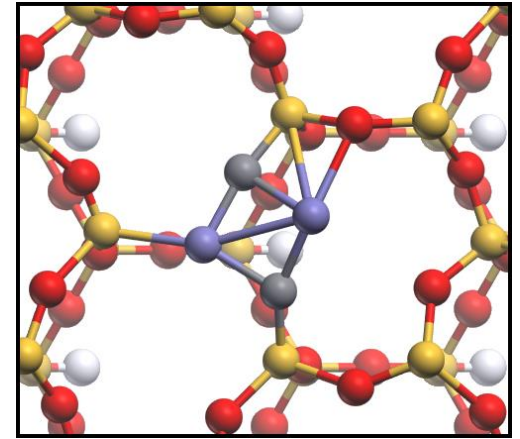
（1）二氧化硅限域的双原子位点设计

(a) $Fe_2©SiO_2$ (b) $Fe_2C©SiO_2$ (c) $Fe_2C_2©SiO_2$
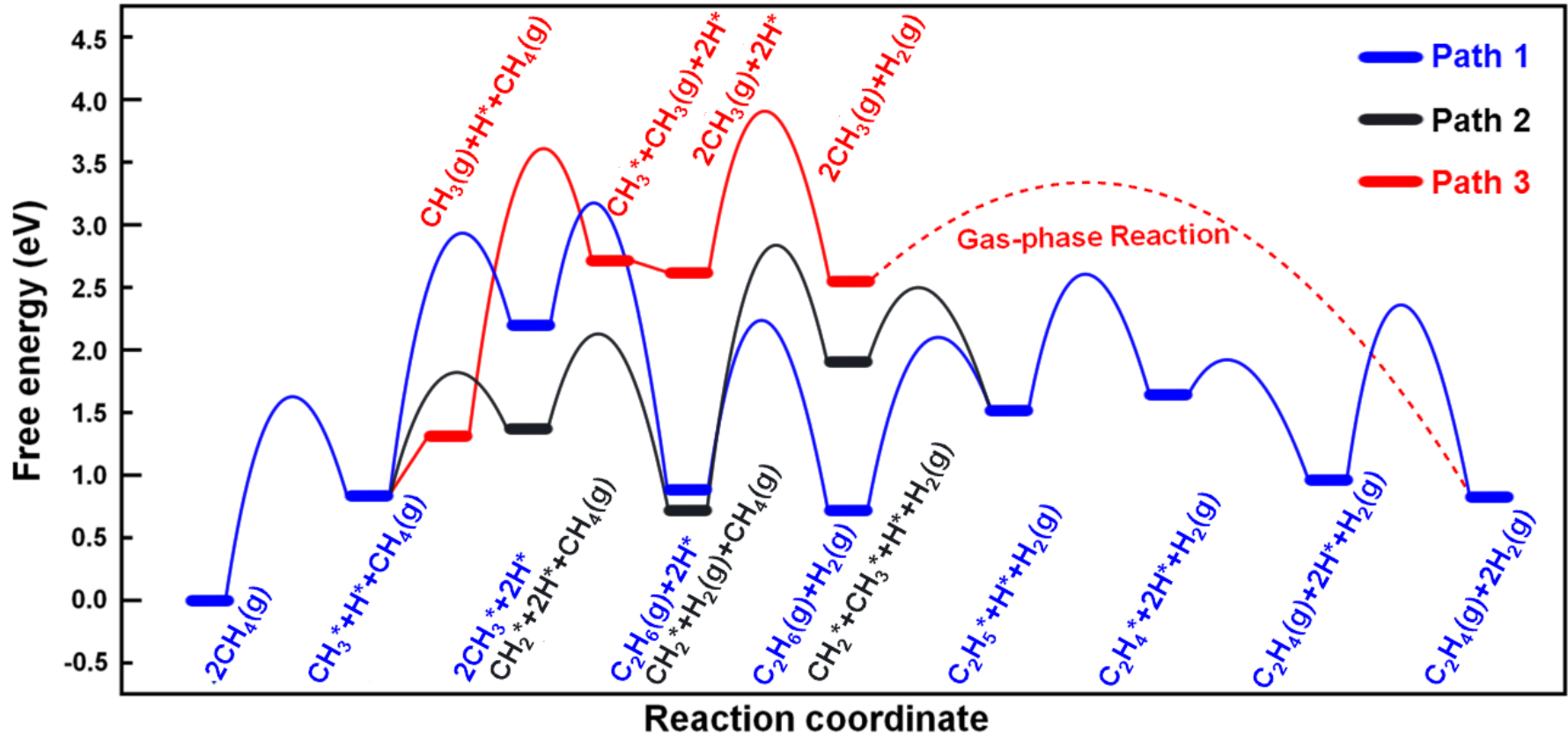
add C atom →

$\triangle G$ (eV) *of* formation of different site from $Fe_2©SiO_2$ and CH_4

| Temperature	$Fe_2©SiO_2$	$Fe_2C©SiO_2$	$Fe_2C_2©SiO_2$
0 K	0.00	0.24	3.45
500 *K*	0.00	-0.26	2.41
1000 *K*	0.00	-0.92	1.04

Fe₂C©SiO₂上甲烷的活化转化

Path 1: CH₃-CH₃ coupling on the surface; Path 2: CH₂-CH₃ coupling on the surface;
Path 3: CH₃ desorbs and reacts in the gas phase

➢ Surface coupling of CHₓ is more favorable than methyl desorption.

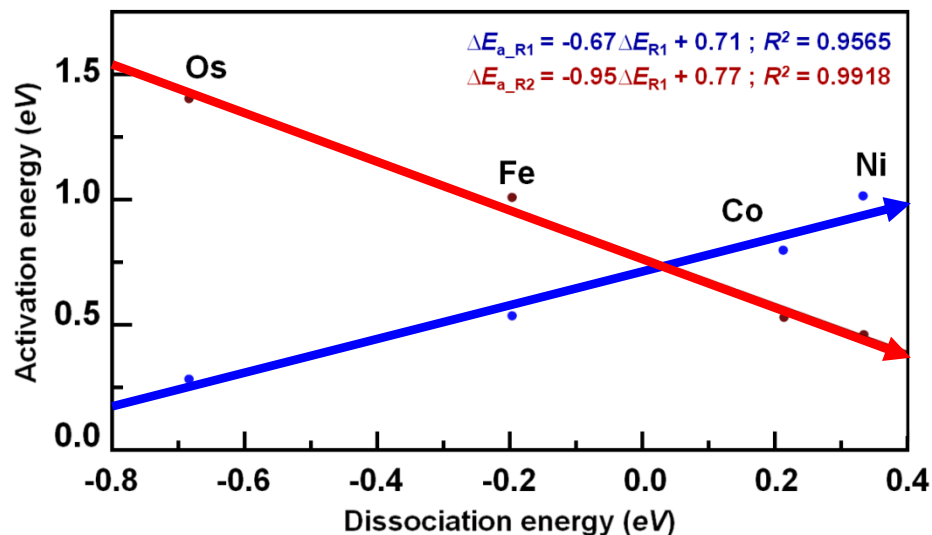➢ CH₂ group can be stabilized, which facilitates C-C coupling.

Fe-M-C©SiO$_2$的筛选及甲烷的活化转化
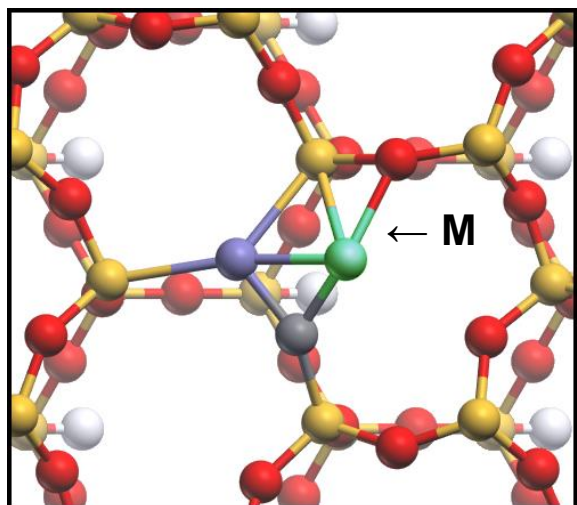
M	ΔE_{R1} / eV	ΔE_{a_R1} / eV	ΔE_{a_R2} / eV
Fe	-0.20	0.53	1.01
Co	0.21	0.79	0.53
Ni	0.33	1.01	0.46
Os	−0.69	0.28	1.40

R1 : $CH_4 \rightarrow CH_3{}^* + H^*$;   R2 : $2CH_3{}^* \rightarrow C_2H_6$
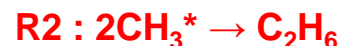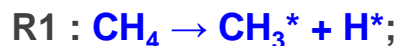
➤ **All di-metal-atom catalysts are better than single-atom ones**

➤ **Strongly exothermic ΔE of CH$_4$ dissociation benefits the activation of CH$_4$, but disfavors C-C coupling.**

（2）石墨烯限域的双原子催化剂设计
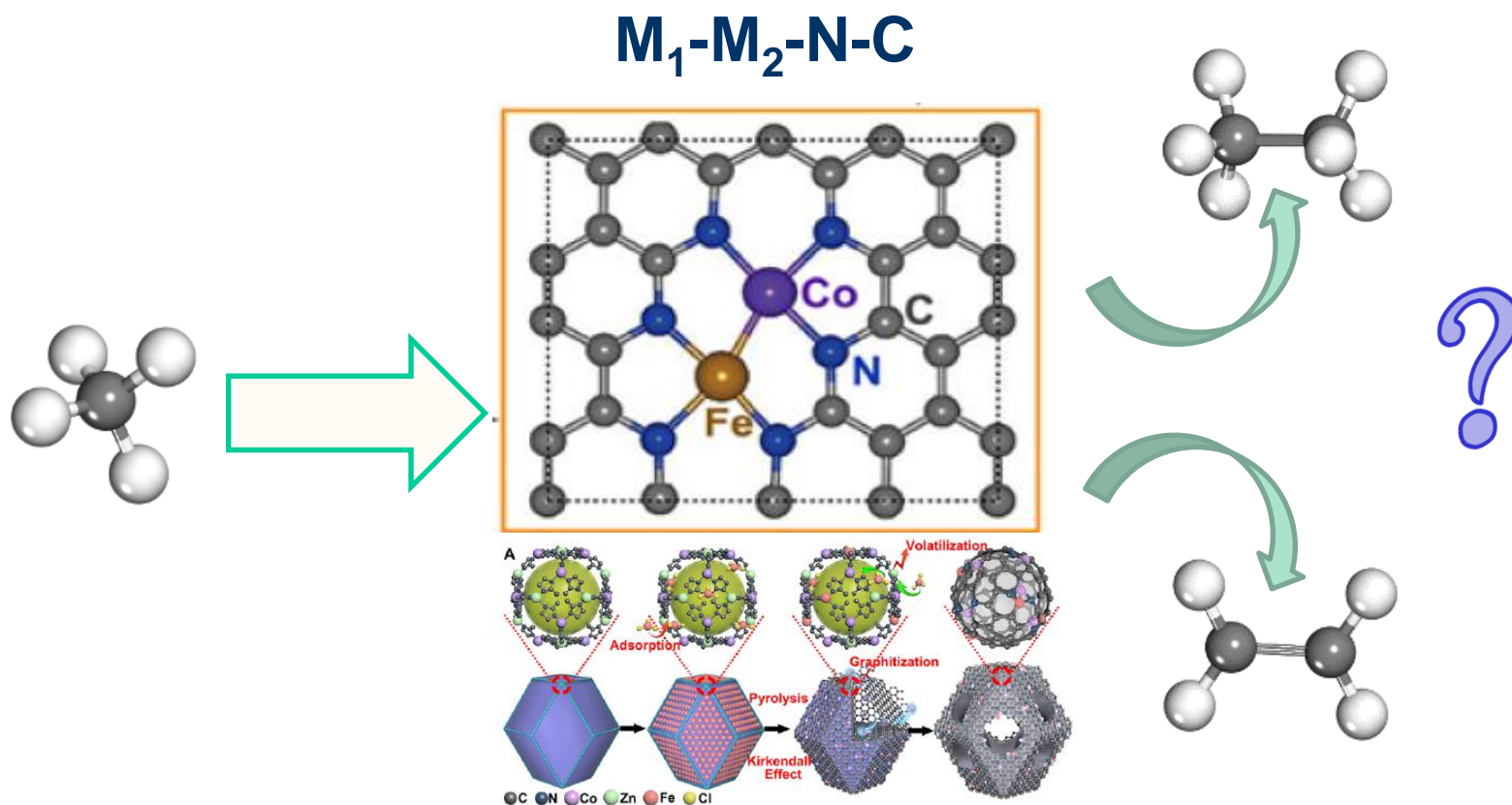
M$_1$-M$_2$-N-C

Wang, Chang*, Wu*, et al., *J. Am. Chem. Soc. 2017, 139, 17281. (citation: 865)*
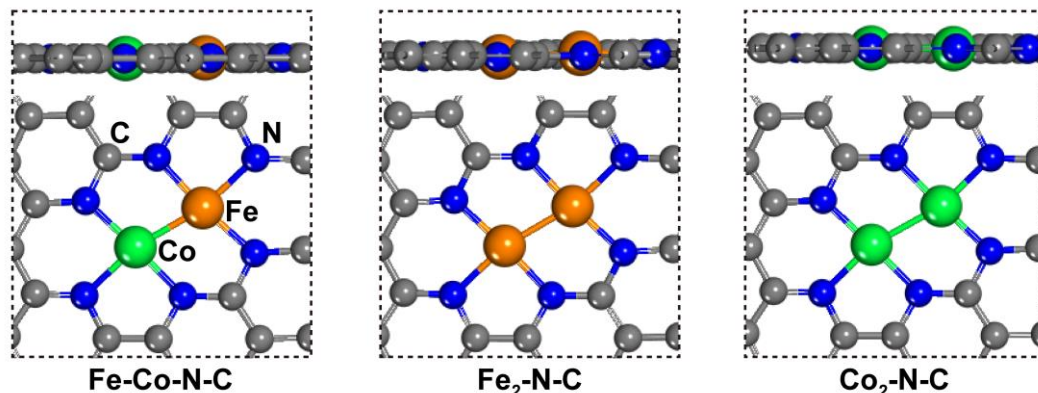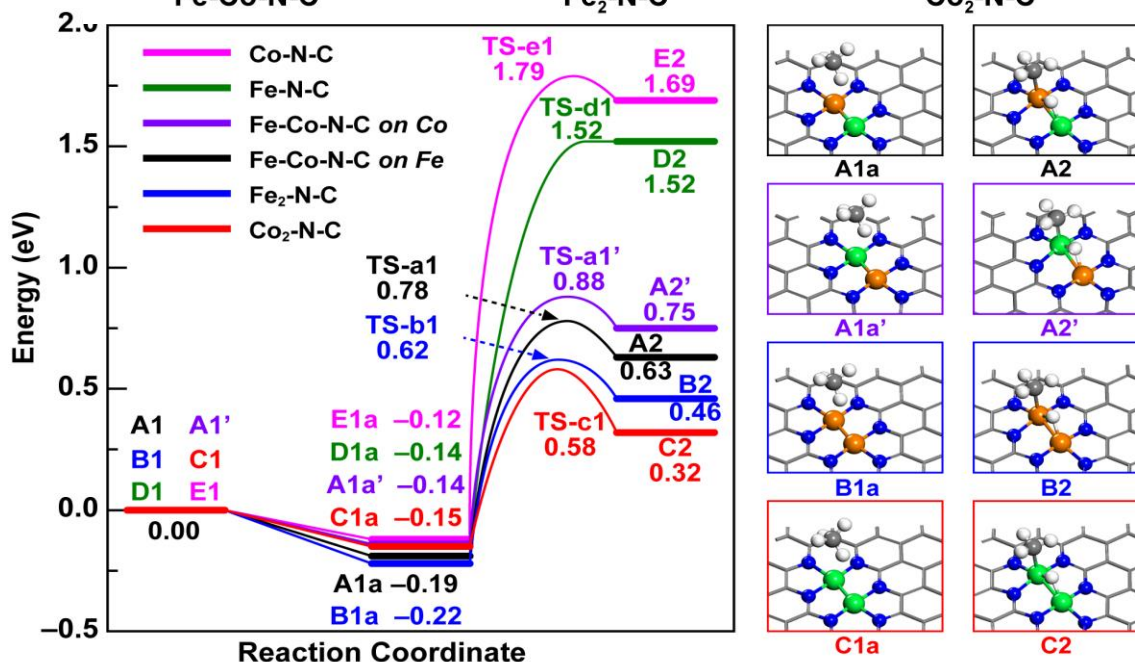
M1-M2-N-C双原子催化剂用于甲烷活化

双原子催化剂模型

Fe-Co-N-C   Fe₂-N-C   Co₂-N-C

甲烷解离活化性能比较

Activation barrier：Co₂-N-C < Fe₂-N-C < Fe-Co-N-C < Fe-N-C < Co-N-C

甲烷在M1-M2-N-C催化剂上的活化转化

$2CH_4 \leftrightarrow 2CH_3^* + H_2$ at 1200 K

$2CH_3^* \leftrightarrow C_2H_4 + H_2$ at 1200 K
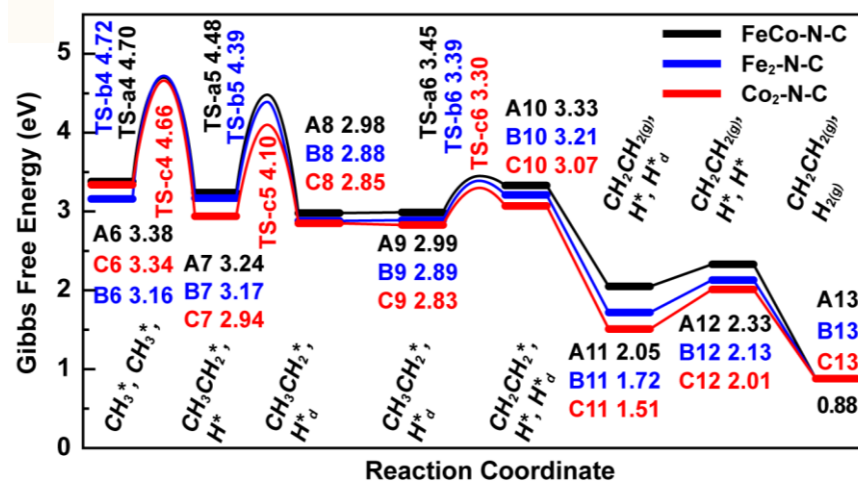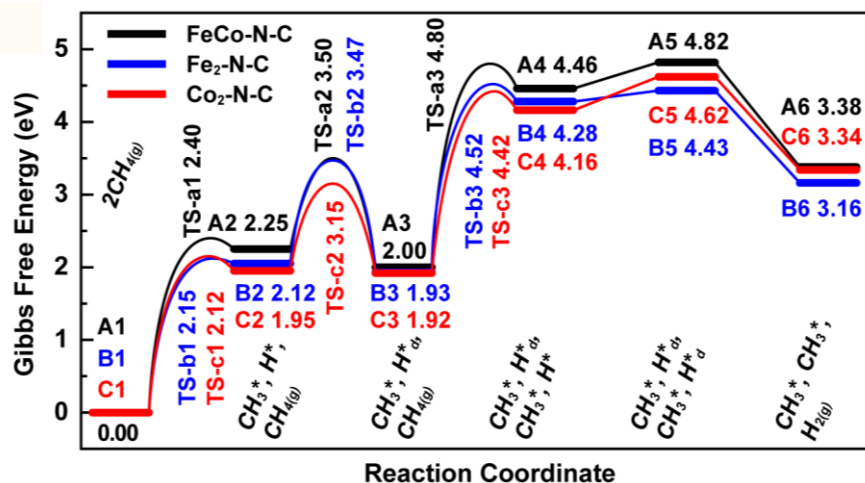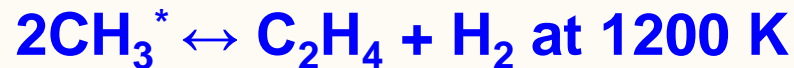
➢ **Co$_2$-N-C presents the best activity for methane conversion.**

➢ **The rate-determining step (RDS) is the dissociation of the 2nd methane.**

➢ **Reaction barriers of RDS at 1200 K:**
Co$_2$-N-C(2.24 eV) < Fe$_2$-N-C(2.36 eV) < Fe-Co-N-C(2.46 eV).

Z.-Q. Huang, C.-R. Chang*, J. Li, ACS Catal., 2021, 11, 13149.

反应网络的微观反应动力学模拟
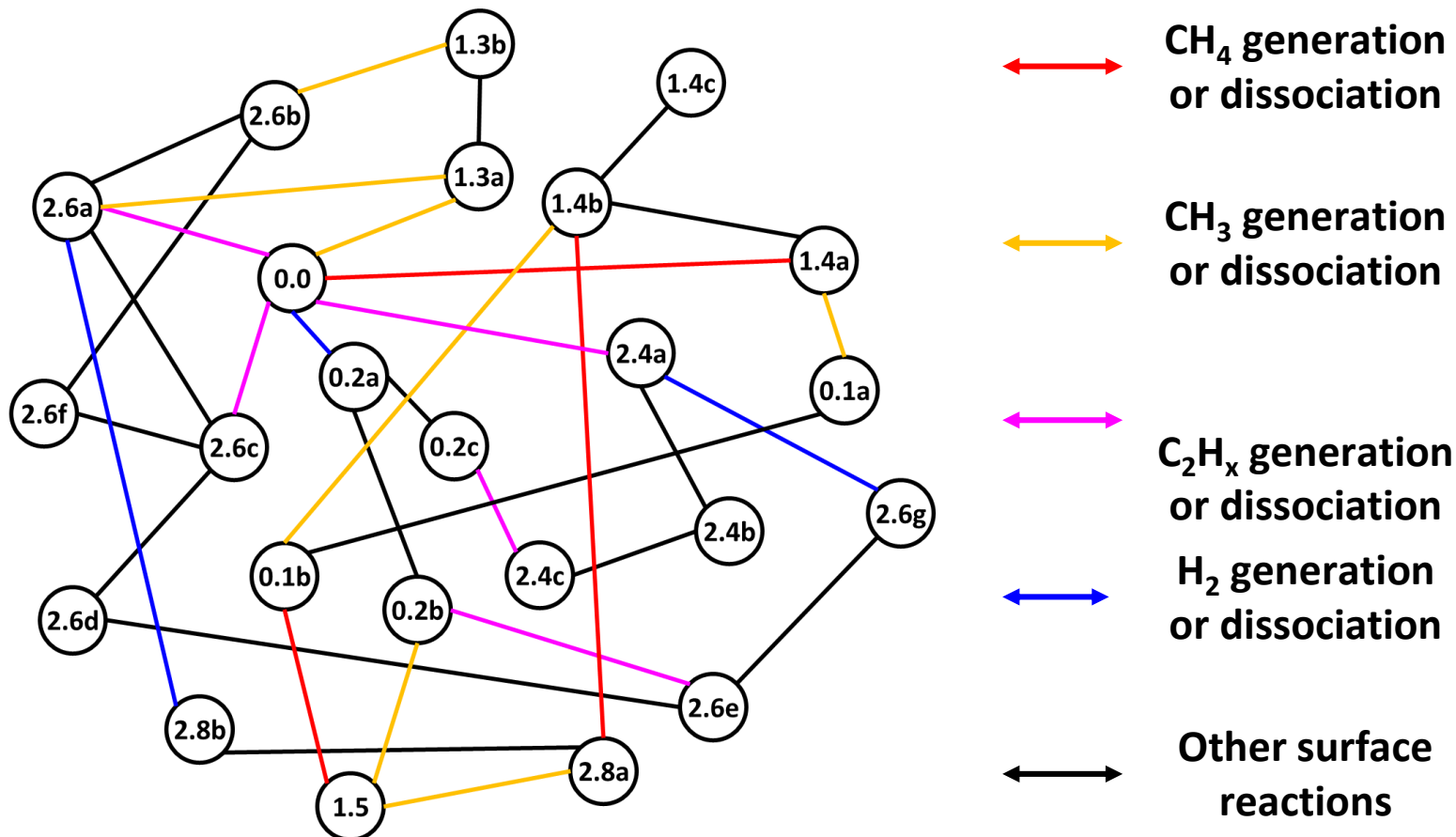
> **The structural notation is based on the number of C and H atoms on active sites.**

> **The reactions involving CH$_3$ is also studied in microkinetic modeling.**

Z.-Q. Huang, C.-R. Chang*, J. Li, ACS Catal., 2021, 11, 13149.

微观反应动力学模拟结果

$$CH_4 \rightarrow C_2H_6 + C_2H_4 + C_2H_2 \text{ at } 1200 \text{ K}$$
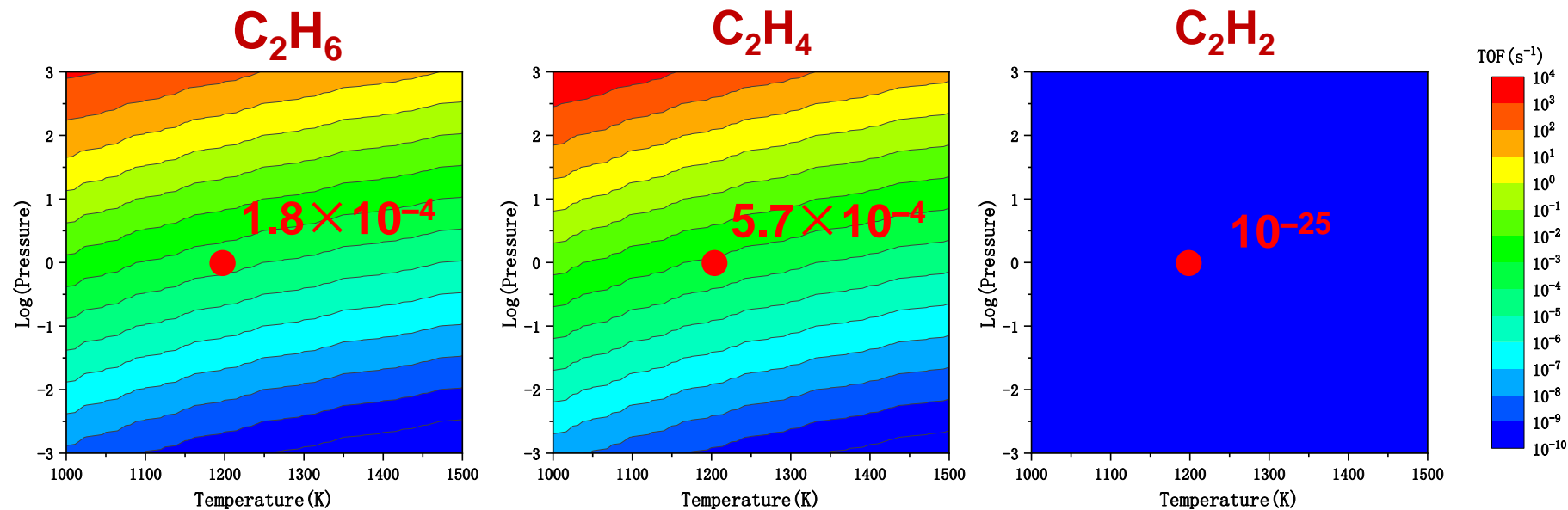
➤ **Nonoxidative coupling of methane on Co_2-N-C at 1200 K can occur with a C_2H_4 production rate of 5.7×10^{-4} s^{-1} (close to the experimental values $\sim 10^{-3}$ s^{-1} over Pt/CeO_2 catalysts, ACS Catal. 2018, 8, 4044).**

Z.-Q. Huang, C.-R. Chang*, J. Li, ACS Catal., 2021, 11, 13149.

Co$_2$-N-C的热力学稳定性分析

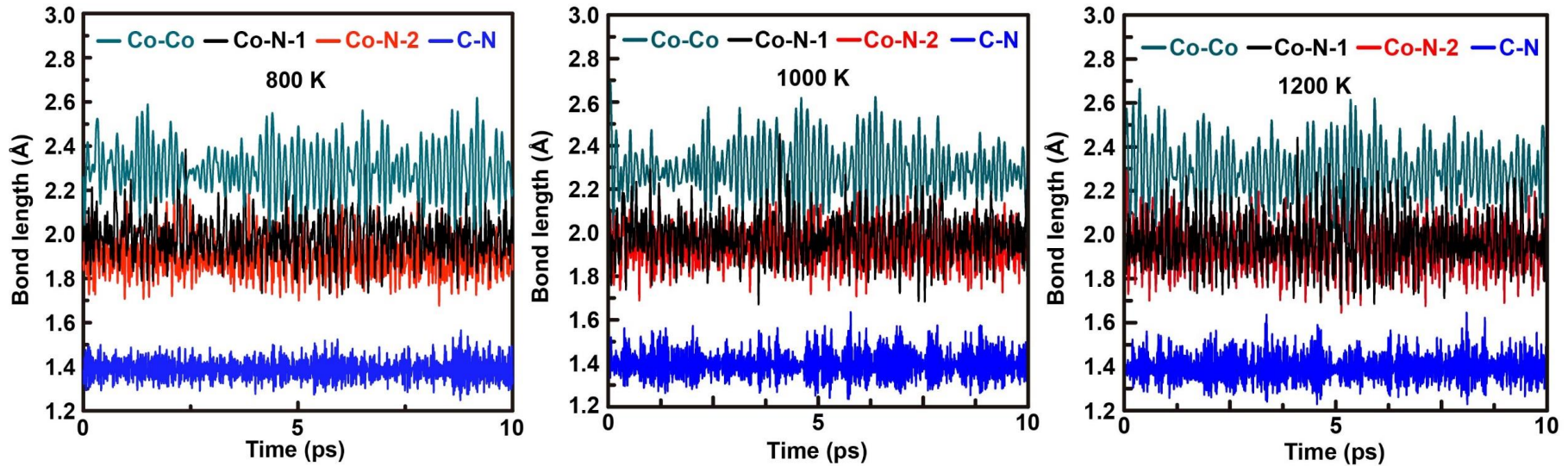| Structures	Bond	800 K		1000 K		1200 K	
		Mean (Å)	Standard Deviation	Mean (Å)	Standard Deviation	Mean (Å)	Standard Deviation
Co-Co-N-C	Co-Co	2.29	0.11	2.28	0.13	2.30	0.12
	Co-N1	1.90	0.08	1.94	0.10	1.94	0.08
	Co-N2	1.99	0.10	1.98	0.11	1.98	0.10
	C-N	1.39	0.04	1.40	0.06	1.40	0.06

Co-Co-N-C is stable at high temperatures

Co₂-N-C的抗积碳性能分析
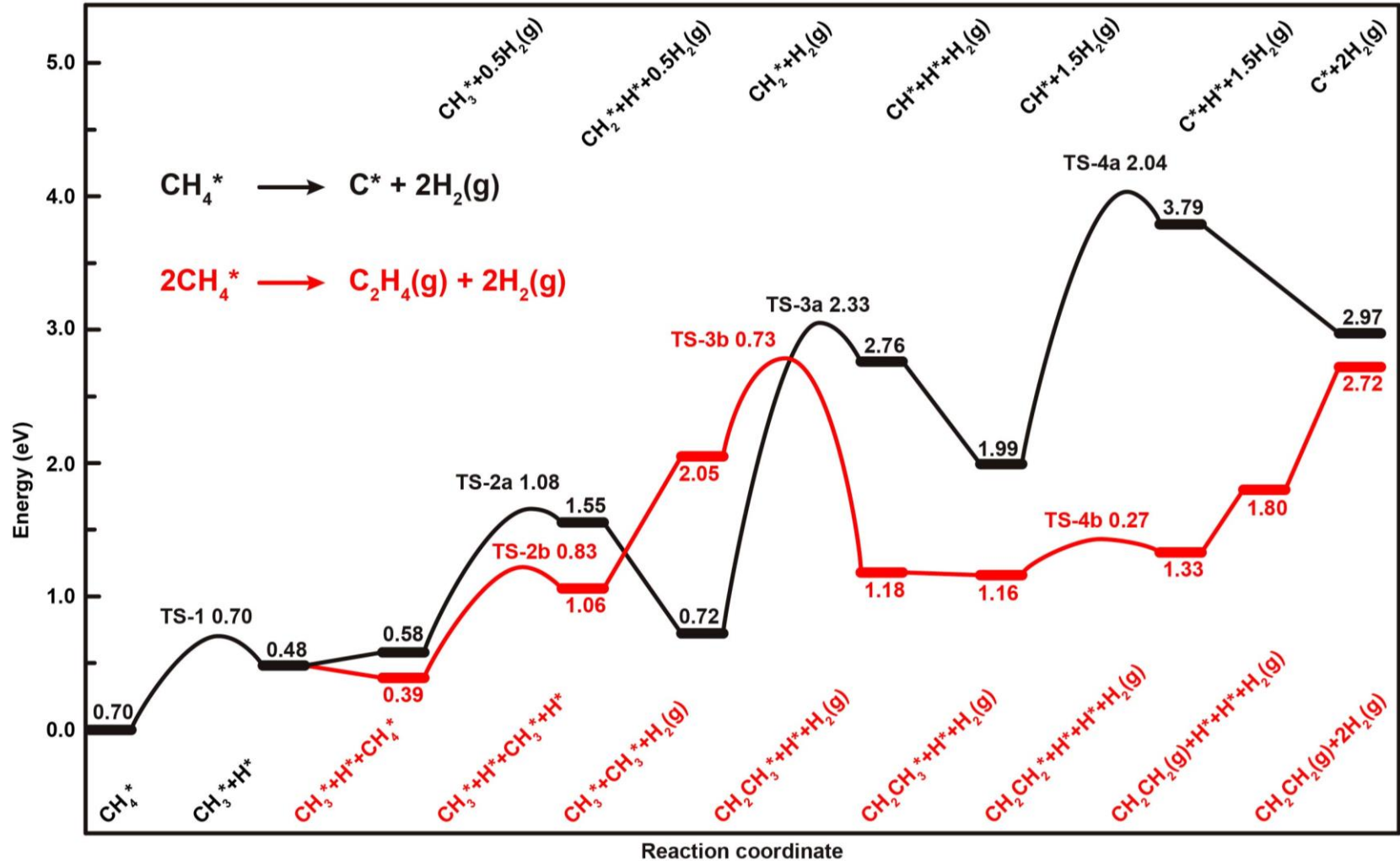
Co₂-N-C presents good performance for coke resistance

结 论

☐ **单铁活性中心的形成机制**

   – 揭示了 活性中心$Fe©SiC_2$的动态形成机制

   – 发现6种其它可能伴随产生的活性位点

☐ **单铁活性中心催化甲烷无氧转化的动态机理**

   – 发现纯气相机理不利于高选择性生成乙烯

   – 揭示了甲烷在$Fe©SiC_2$表面生成C2物种的"类MvK"机理

☐ **新型单/多活性中心催化剂的设计及构-效关系**

   – 理论筛选出性能更优的$W©SiC_2$单原子中心催化剂

   – 理论设计出$Fe_2C©SiO_2$、Co_2-N-C等双原子中心催化剂

总 结

Experiments

"real" Experiments (practical ways)

(1) Always "right" in sighting/vision

(2) Possible "wrong" in analysis/explain

"virtual" Experiments (theoretical ways)

(1) Possible "wrong" in tools/models

(2) Possible "right" in analysis/prediction

Better Understanding

Virtual experiments are to design/predict (first priority task), and to explain!
Real experiments can confirm the designs or predictions, and make reality!

Problem is how to combine together!

致 谢

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N S F C

"碳基能源转化利用的催化科学"重大研究计划

Thanks for your attention!