Supporting Information

of

Reconstruction of Wet Chemical Synthesis Process: The Case of Fe_5C_2 Nanoparticles

Siyu Yao[1]‡, Ce Yang[1, 2]‡, Huabo Zhao[1], Siwei Li[1], Lili Lin[1], Wen Wen[3], Jinxun Liu[4], Gang Hu[5], Weixue Li[4], Yanglong Hou[2] and Ding Ma[1]**

1. College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

2. College of Engineering, Peking University, Beijing 100871, China.

3. Shanghai Institute of Applied Physics, Chinese Academy of Science, Shanghai Synchrotron Radiation Facility (SSRF), Shanghai 201204, China

4. Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China; State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

5. Israel Chemicals Limited, Shanghai, 200021, China

FIGURES AND TABLES

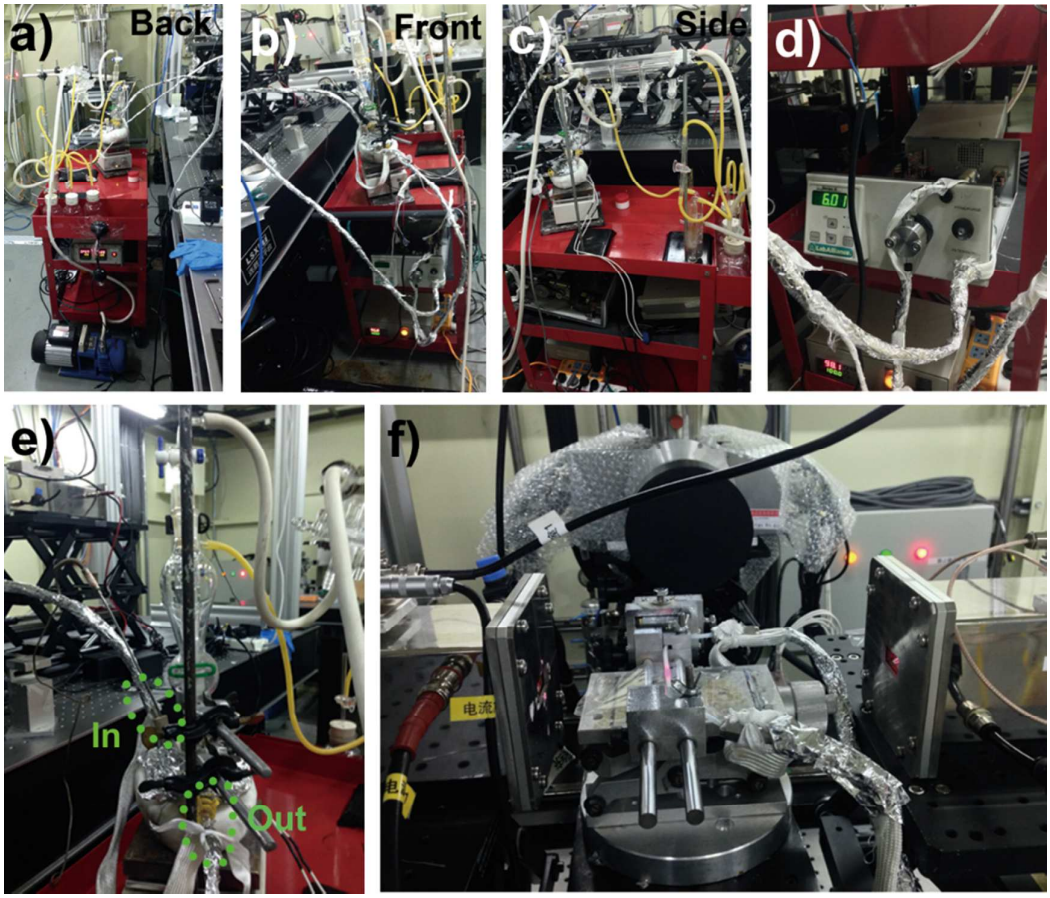

Figure S1. Setup of in-situ characterization system. a) back, **b)** Front and **c)** side views of the system. **d)** image for piston pump. **e)** close-up image for the liquid-in and out part of the reaction. **f)** image for the home-made cell.

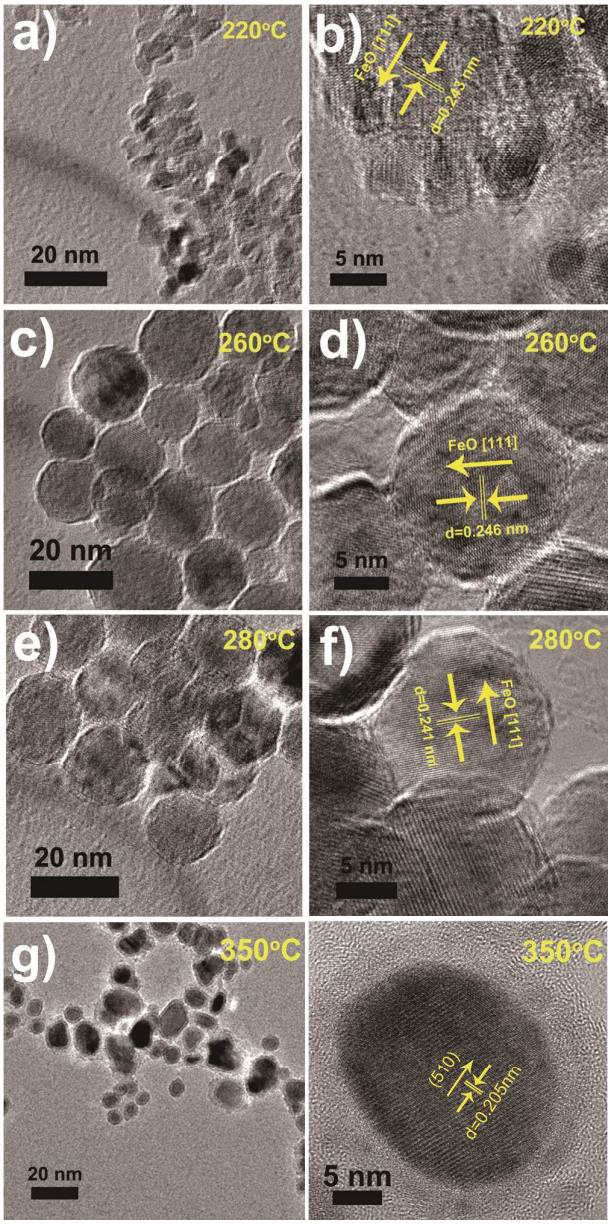

Figure S2. TEM and HRTEM images of NPs obtained when the reaction reached **a,b)** 220°C, **c,d)** 260°C and **e,f)** 280°C. **g,h)** 350°C

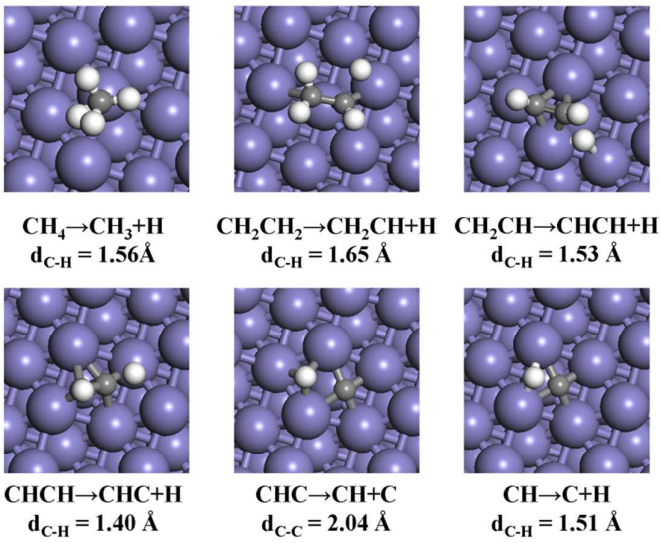

Figure S3. The transition states (TSs) geometries involved in methane and ethene dissociation process. The bond distances between C-H and C-C at TSs are indicated.

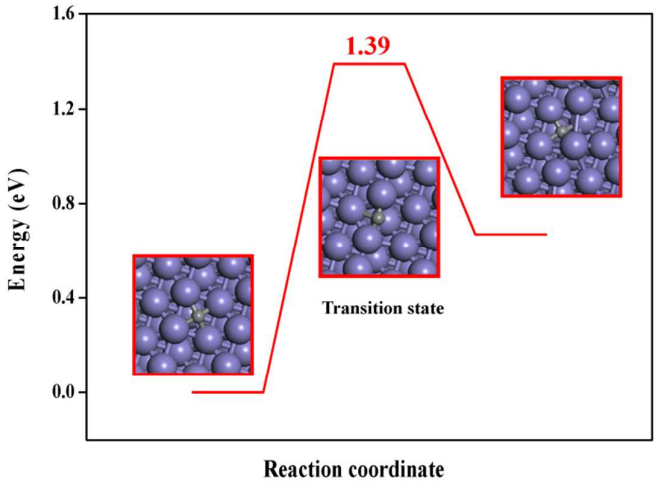

Figure S4. The potential energy diagram for atomic carbon diffusion from Fe surface to subsurface. The barrier (in eV) and configurations of initial state, transition state and final state involved are indicated. Fe surface have been reconstructed for the final state.

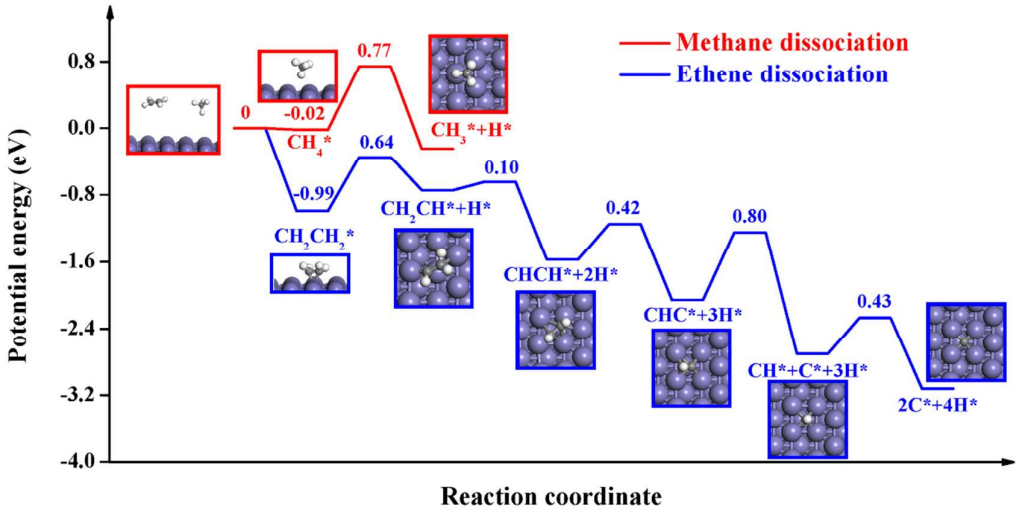

Figure S5. Potential energy diagram and the favorable adsorption configurations of key intermediates for methane and ethene dissociation on Fe (310) step surface. Methane, ethene adsorption energies and the elementary reaction barriers are indicated. Purple, grey and white balls are Fe, C and H atoms.

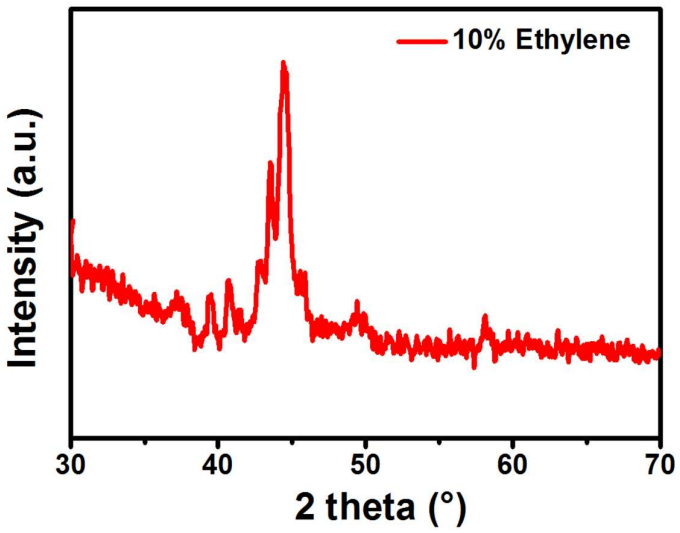

Figure S6. XRD patterns of product generated from a control experiment which was designed by holding the temperature of the synthetic system at 300°C and then diluted ethylene (10% C2H4/90% Ar) was bubbled into the high temperature organic solution for 30 min. The XRD profiles suggested that the product thus generated was Fe5C2.

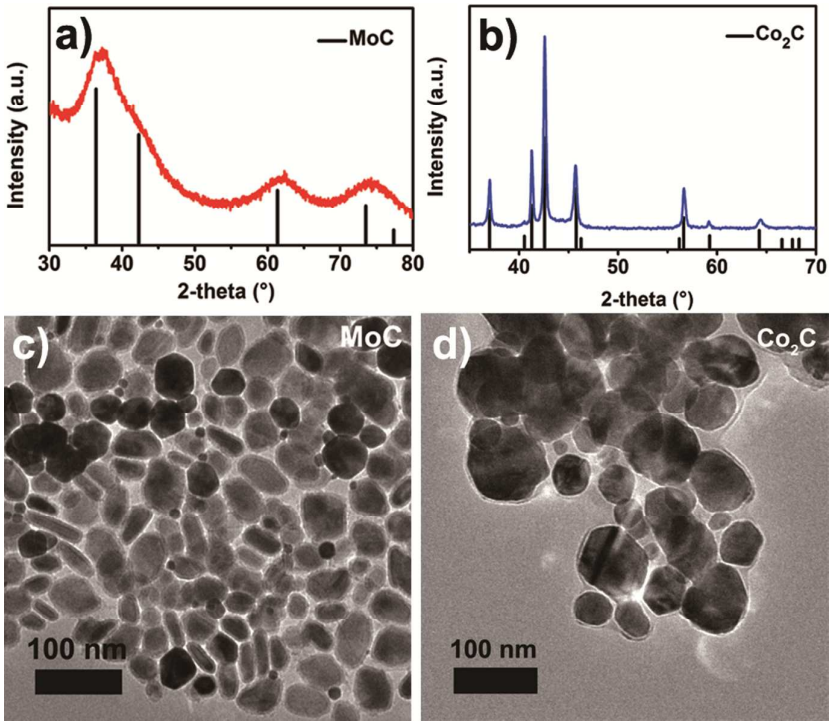

Figure S7 (a, b) XRD pattern and **(c,d)** TEM images of MoC and Co_2C NPs. The black lines in XRD profiles are standard patterns of MoC (JCPDS No. 89-2868) and Co_2C (JCPDS No. 05-0704).

Table S1. Fe K edge EXAFS fitting results of the synthetic system at different temperature

Entry	Sample	Shell	R (Å)[a]	C.N.[b]	σ^2 (Å^2)[c]	E_0 shift (eV)[d]
1	180_1[e]	Fe-C	1.81±0.01	2.7±0.8	0.002	1.9
		Fe-Fe	2.53±0.01	0.7±0.4	0.008	
		Fe-Fe	2.75±0.01	6.0±1.7	0.012	
2	180_2[f]	Fe-O	2.06±0.03	3.8±1.4	0.010	4.0
		Fe-Fe	2.50±0.02	1.5±0.5	0.008	
		Fe-Fe	3.08±0.02	6.8±2.4	0.013	
3	220	Fe-O	2.11±0.02	5.8±1.7	0.011	0.5
		Fe-Fe	2.50±0.01	0.8±0.2	0.007	
		Fe-Fe	3.08±0.02	8.1±1.5	0.011	
4	240	Fe-O	2.08±0.01	6.9±1.6	0.020	-1.7
		Fe-Fe	3.07±0.01	10.2±1.2	0.012	
5	260	Fe-O	2.10±0.02	6.8±1.7	0.011	-3.0
		Fe-Fe	3.07±0.01	12.4±1.5	0.012	
6	280	Fe-Fe	2.44±0.02	3.0±1.0	0.006	-5.7
		Fe-Fe	2.79±0.02	2.3±0.7	0.006	
7	300	Fe-Fe	2.44±0.02	4.5±1.4	0.012	-2.7
8	320	Fe-C	1.90±0.05	0.7±0.5	0.006	-5.6
		Fe-Fe	2.46±0.01	4.0±0.6	0.012	
9	340	Fe-C	1.99±0.01	5.1±0.7	0.007	-7.1
		Fe-Fe	2.60±0.01	9.6±1.8	0.014	
10	350	Fe-C	1.99±0.01	3.5±1.4	0.008	-6.9
		Fe-Fe	2.60±0.01	8.6±1.0	0.015	

a. bond length; b. coordination number; c. Debye-Waller factor; d. difference of inner potential; e. the sample collected 1 min after $Fe(CO)_5$ injection; f. the sample collected after 30 min decomposition at 180 °C.