Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Reduction mechanism of iron titanium based oxygen carriers with H_2 for chemical looping applications- A combined experimental and theoretical study

Yu-Cheng Liu,[a,†] Santhanamoorthi Nachimuthu,[b,†] Yu-Cheng Chuang,[b] Young Ku [a,*] and Jyh-Chiang Jiang [b,*]

[a] *Environmental Engineering Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan, E-Mail:* ku508@mail.ntust.edu.tw

[b] *Computational and Theoretical Chemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan,*

E-Mail: jcjiang@mail.ntust.edu.tw

† These authors contributed equally to this work

Table S1. Typical reaction conditions and results in case of Fe_2TiO_5.

Heating rate (ºC/min)	Reaction Temperature (ºC)	Holding time (hr)	Results
5	600	2	TiO_2, Fe_2O_3
5	700	2	TiO_2, Fe_2O_3
5	800	2	TiO_2, Fe_2O_3
5	900	2	TiO_2, Fe_2O_3, Fe_2TiO_5
5	1000	2	TiO_2, Fe_2O_3, Fe_2TiO_5
5	1025	2	TiO_2, Fe_2O_3, Fe_2TiO_5
5	1050	2	TiO_2, Fe_2O_3, Fe_2TiO_5
5	1075	2	Fe_2TiO_5

Table S2. Typical reaction conditions and results in case of Fe_2TiO_4.

Heating rate (ºC/min)	Reaction Temperature (ºC)	Holding time (hr)	Results
5	900	2	FeO, $FeTiO_3$, Fe_2TiO_4
5	1000	2	FeO, $FeTiO_3$, Fe_2TiO_4
5	1100	2	FeO, $FeTiO_3$, Fe_2TiO_4
5	1200	2	FeO, $FeTiO_3$, Fe_2TiO_4
5	1300	2	FeO, $FeTiO_3$, Fe_2TiO_4
5	1300	5	FeO, $FeTiO_3$, Fe_2TiO_4
5	1325	2	FeO, $FeTiO_3$, Fe_2TiO_4
5	1325	5	Fe_2TiO_4

Table S3. Typical reaction conditions and results in case of $FeTiO_3$.

Heating rate (ºC/min)	Reaction Temperature (ºC)	Holding time (hr)	Results
5	400	2	TiO_2, FeO
5	500	2	TiO_2, FeO, $FeTiO_3$
5	600	2	TiO_2, FeO, $FeTiO_3$
5	625	2	TiO_2, FeO, $FeTiO_3$
5	625	5	TiO_2, FeO, $FeTiO_3$
5	650	2	TiO_2, FeO, $FeTiO_3$
5	650	5	$FeTiO_3$

Table S4. Experimental and Calculated lattice parameters for the bulk structure of three iron titanium oxides.

System	**a (Å)**	**b (Å)**	**c (Å)**
Fe_2TiO_5			
Expt.[1]	3.739	9.779	9.978
Calculated	3.750	9.850	10.04
Fe_2TiO_4[a]			
Expt.[2]	8.534		
Calculated	8.496		
$FeTiO_3$[b]			
Expt.[3]	5.088		14.092
Calculated	5.075		14.036

[a:] lattice constant a = b = c

[b:] lattice constant a = b ≠ c

Table S5. The observed rate constants (k_{obs}) and the reaction orders (n) for the reduction of three iron titanium oxides (Fe_2TiO_5, Fe_2TiO_4, and $FeTiO_3$) with H_2 molecule at various reaction temperatures.

Structure	Temperature (°C)	k_{obs}	n
Fe_2TiO_5	800	8.36×10^{-3}	0.71
	850	1.09×10^{-2}	
	900	1.32×10^{-2}	
	950	1.59×10^{-2}	
	1000	1.84×10^{-2}	
Fe_2TiO_4	800	6.16×10^{-4}	0.54
	850	1.06×10^{-3}	
	900	1.58×10^{-3}	
	950	2.19×10^{-3}	
	1000	2.66×10^{-3}	
$FeTiO_3$	800	3.03×10^{-5}	0.27
	850	5.22×10^{-5}	
	900	1.03×10^{-4}	
	950	1.35×10^{-4}	
	1000	2.04×10^{-4}	

Table S6. Calculated intermolecular distances (in Å) and imaginary Frequencies (IMF, cm^{-1}) for three iron titanium oxides (Fe_2TiO_5, Fe_2TiO_4, and $FeTiO_3$) during the reduction mechanism.

System	Surface				H_2O		
	H-H	**Fe-H**	**H-O**	**Fe-O**	**H-O_1**	**H-O_2**	**IMF**
Fe_2TiO_5							
IS	0.797	0.173	2.121	1.885			
TS1	0.930	1.635	1.382	2.081			*i*831
IM	1.991	1.490	0.977	2.114			
TS2	2.172	1.489	0.967	2.853			*i*1157
FS					0.982	0.982	
Fe_2TiO_4							
IS	0.823	1.771	2.611	1.950			
TS1	1.004	1.695	1.335	2.137			*i*895
IM	2.471	1.500	0.976	1.955			
TS2	1.182	1.775	1.428	2.783			*i*1382
FS					0.979	0.985	
$FeTiO_3$[b]							
IS	0.754	2.696	2.921	2.046			
TS1	1.309	1.663	1.045	2.611			*i768*
IM	2.864	1.762	0.977	2.221			
TS2	1.994	2.092	1.089	2.461			*i*1056
FS					1.013	0.988	

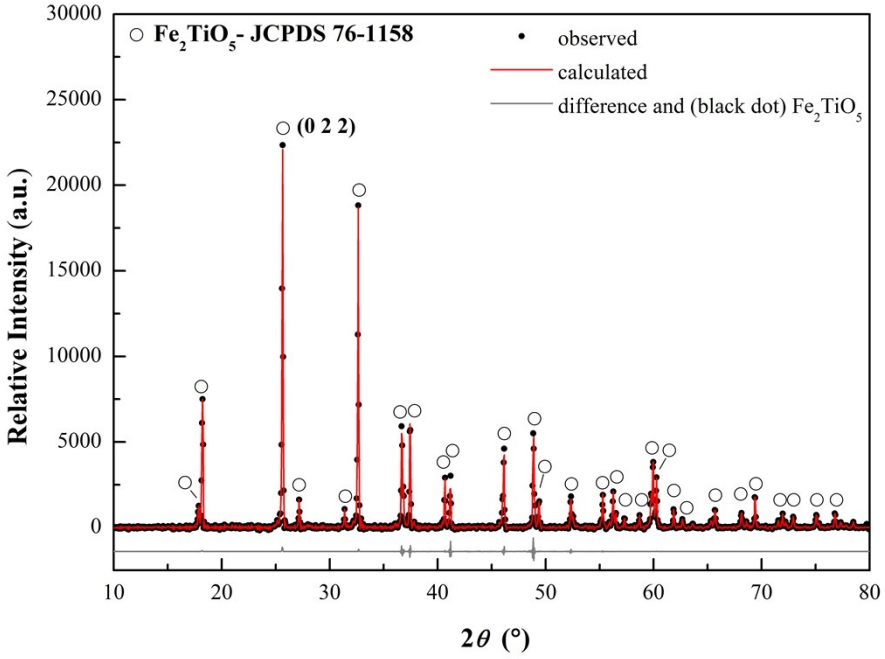


Figure S1. The XRD patterns for Fe_2TiO_5. The upper symbols illustrate the observed data (black dot), calculated pattern (red line) and the difference between them (grey line).

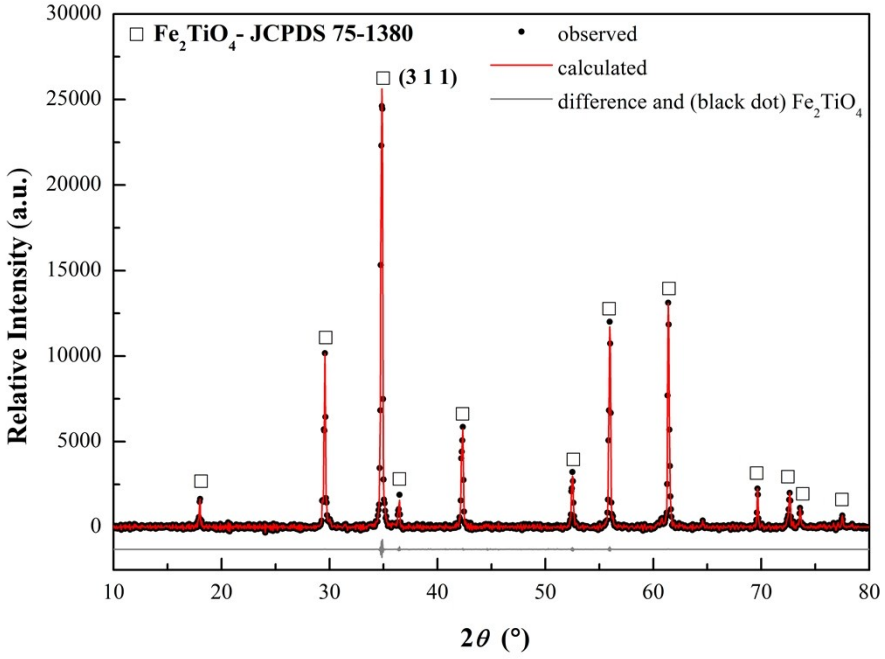


Figure S2. The XRD patterns for Fe_2TiO_4. The upper symbols illustrate the observed data (black dot), calculated pattern (red line) and the difference between them(grey line)

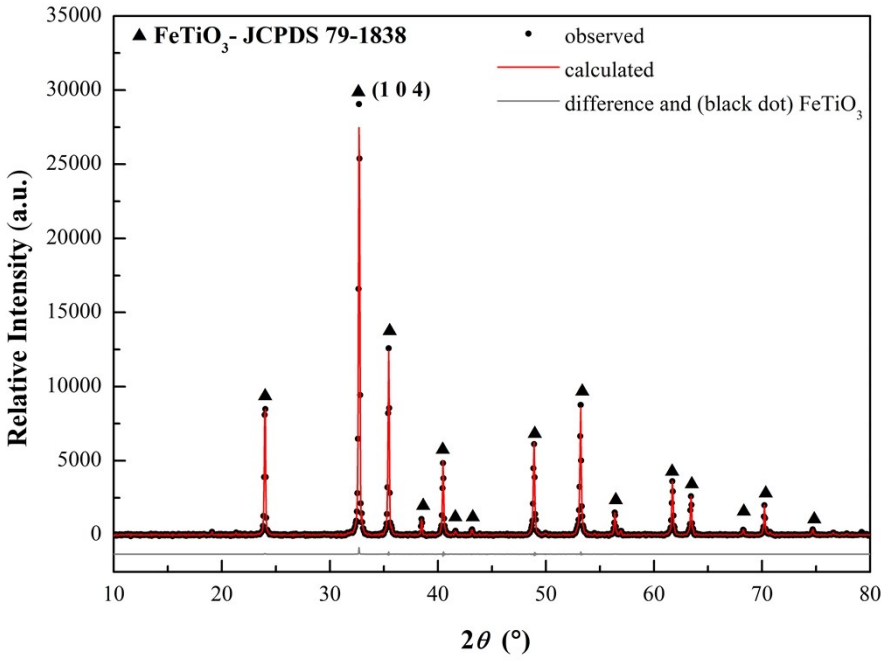
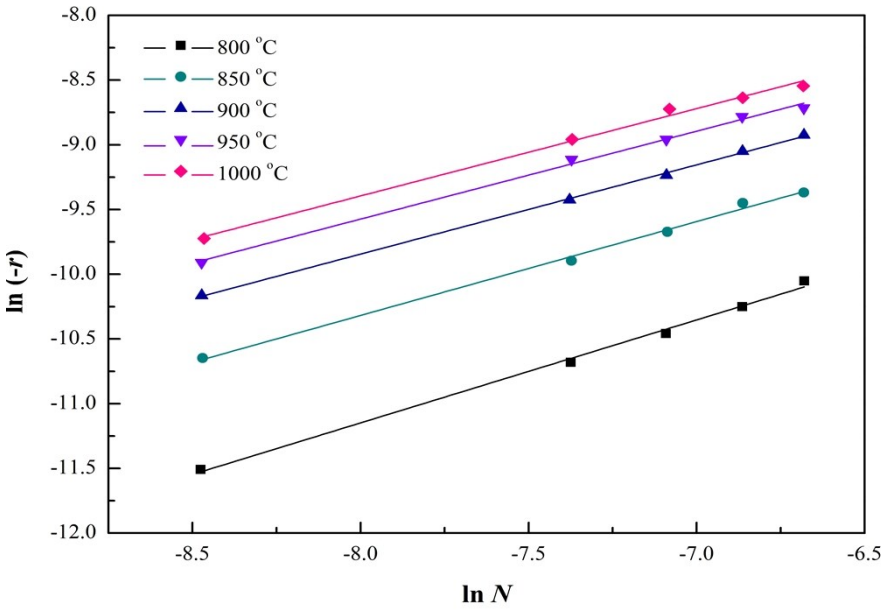
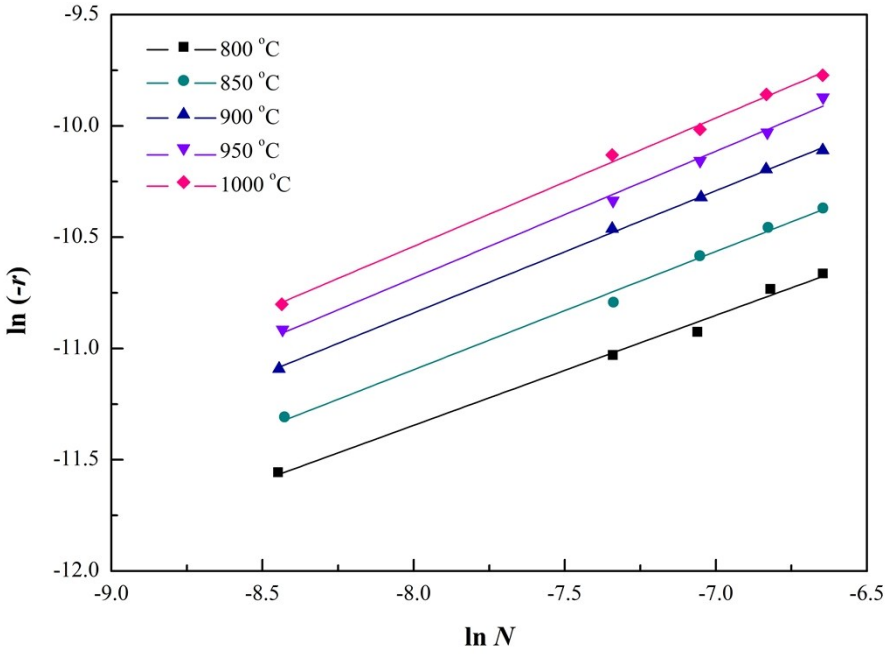


Figure S3. The XRD patterns for $FeTiO_3$. The upper symbols illustrate the observed data (black dot), calculated pattern (red line) and the difference between them (grey line).

(a)


800 °C
850 °C
900 °C
950 °C
1000 °C
ln (-r)
ln N
-8.0
-8.5
-9.0
-9.5
-10.0
-10.5
-11.0
-11.5
-12.0
-8.5
-8.0
-7.5
-7.0
-6.5

(b)


800 °C
850 °C
900 °C
950 °C
1000 °C
ln (-r)
ln N
-9.5
-10.0
-10.5
-11.0
-11.5
-12.0
-9.0
-8.5
-8.0
-7.5
-7.0
-6.5

(c)

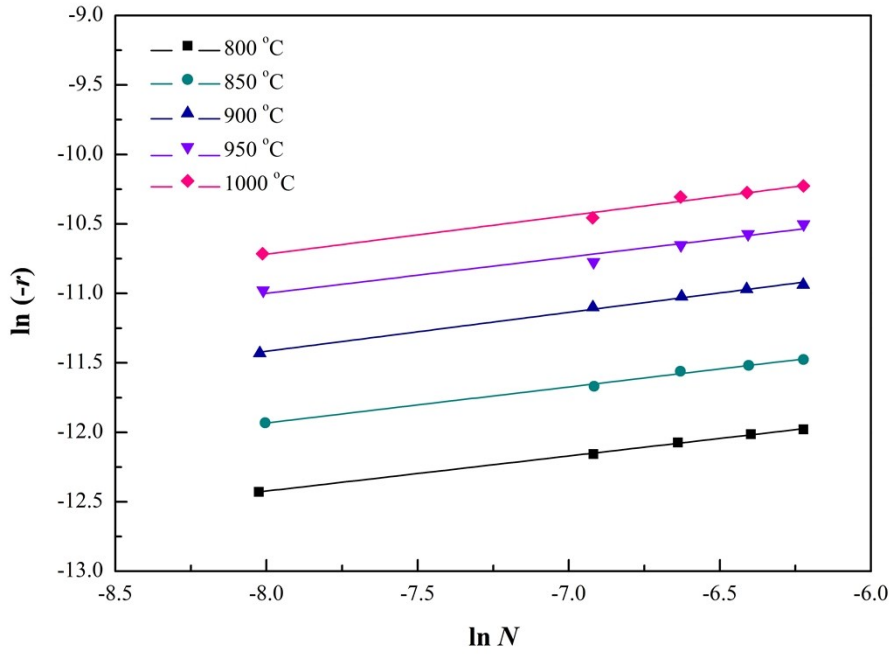


Figure S4. Reactivity curves by TGA from 800-1000 °C using 20.4 % of H_2 as fuel. Fitting lines correspond to results predicted by the model using kinetic parameters from (a) Fe_2TiO_5, (b) Fe_2TiO_4, and (c) $FeTiO_3$ reduction.

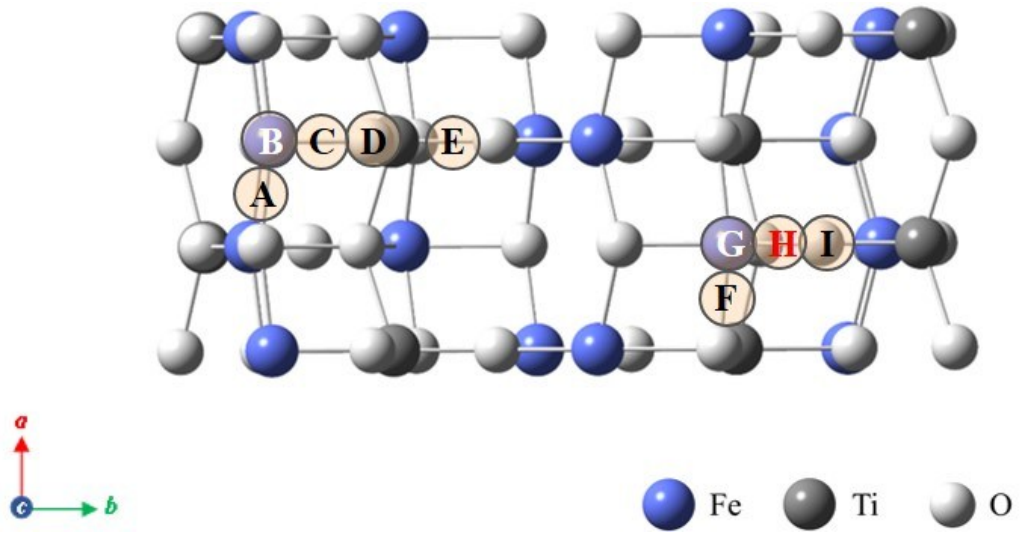


Figure S5. The considered different adsorption sites for the H_2 molecule on Fe_2TiO_5 (0 2 2) surfaces.

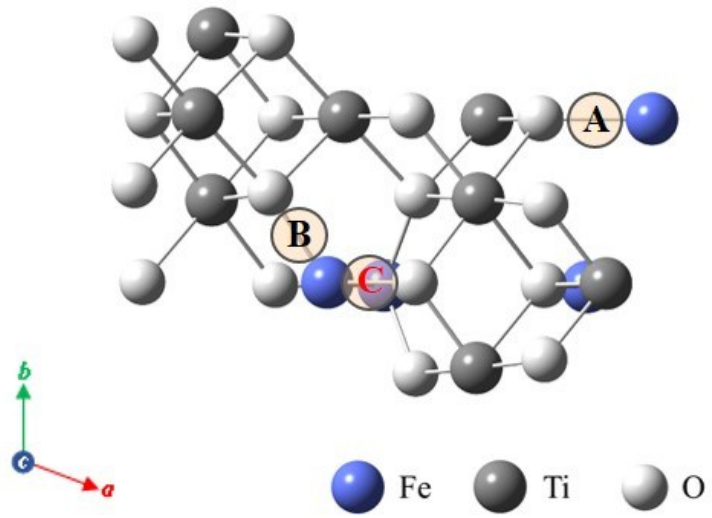


Figure S6. The considered different adsorption sites for the H_2 molecule on Fe_2TiO_4 (3 1 1) surface

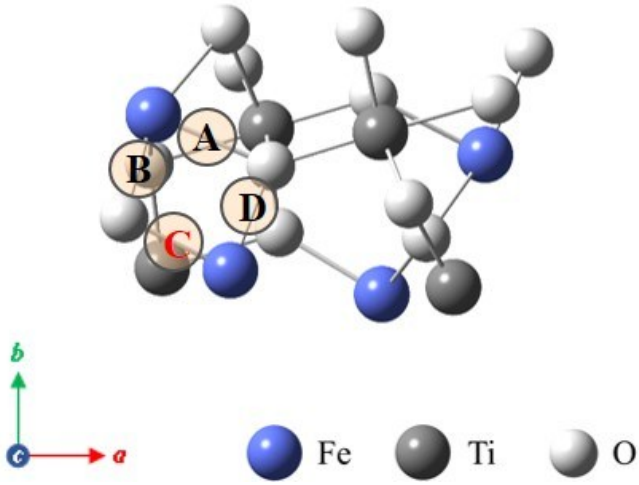
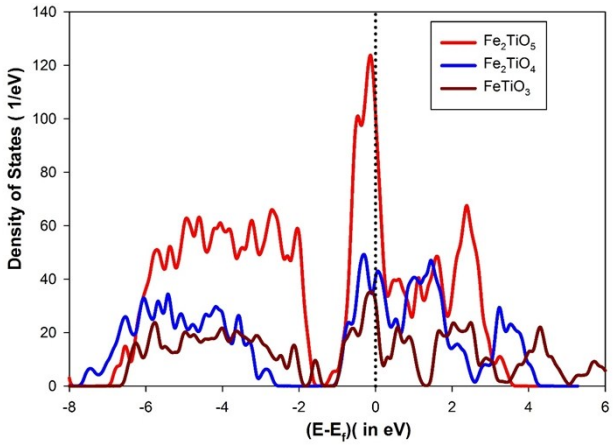
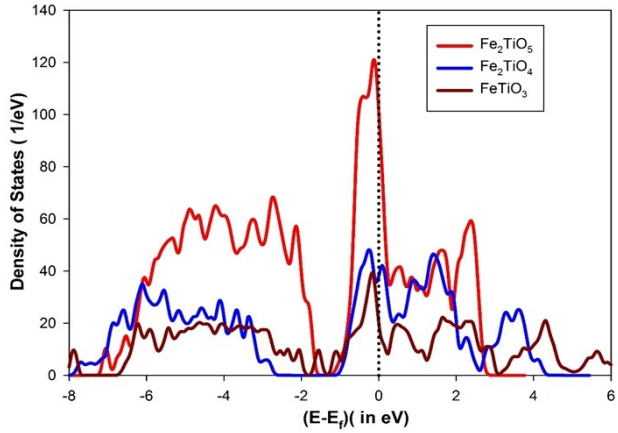


Figure S7. The considered different adsorption sites for the H_2 molecule on $FeTiO_3$ (1 0 4) surface

(a)



(b)



(c)

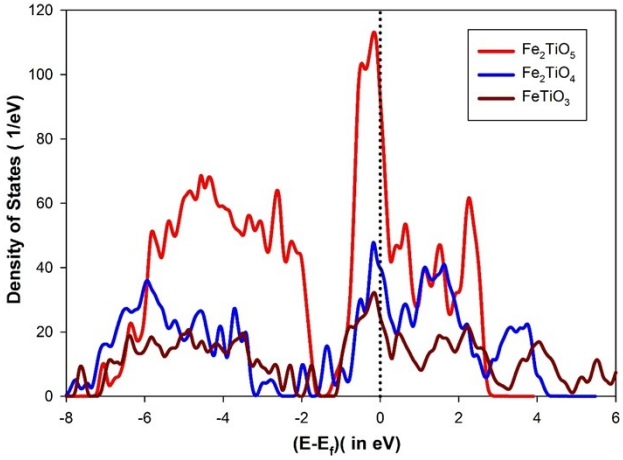
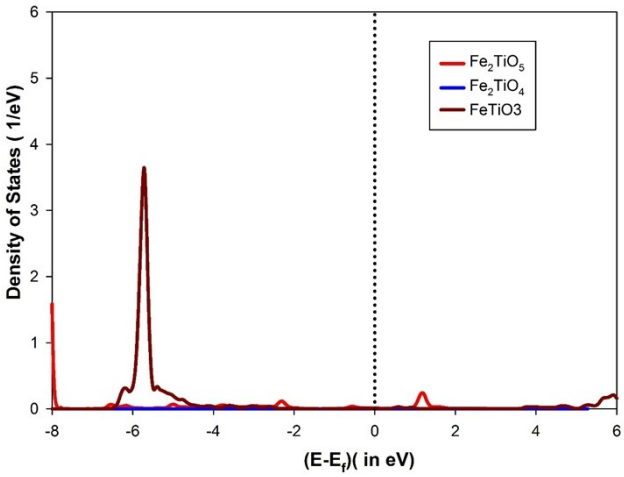
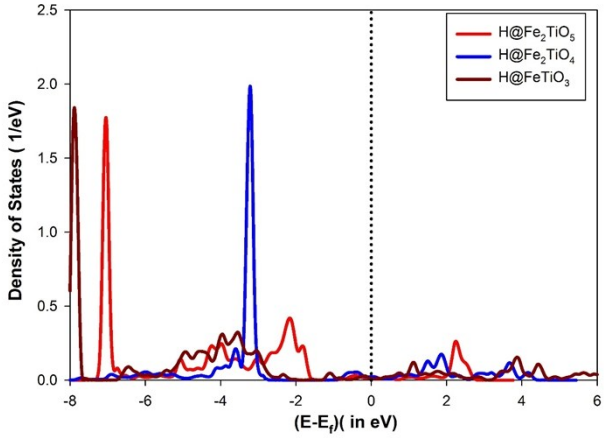


Figure S8. Total density of states of H_2 adsorbed on the three oxygen carriers ((a) when H_2 adsorbed on the surfaces in IS, (b) when adsorbed H_2 dissociates into H atoms in IM and (c) when H_2O formed on the surfaces in FS.)

(a)



(b)



(c)

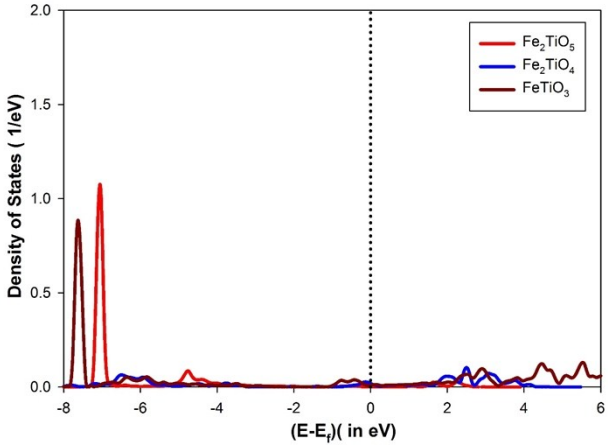


Figure S9. Partial density of states of H_2 after adsorbed on the three oxygen carriers ((a) when H_2 adsorbed on the surfaces in IS, (b) when adsorbed H_2 dissociates into H atoms in IM and (c) when H_2O formed on the surfaces in FS.)

References:

1. P. Tiedemann and H. Müller-Buschbaum, *Zeitschrift für anorganische und allgemeine Chemie*, 1982, **494**, 98-102.
2. B. A. Wechsler, D. H. Lindsley and C. T. Prewitt *Americal Mineralogist*, 1984, **69**, 754.
3. K. N. Raymond and H. R. Wenk, *Contributions to Mineralogy and Petrology*, **30**, 135-140.