Supporting Information for

Excess Charge Driven Dissociative Hydrogen Adsorption on Ti₂O₄⁻

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Fig. S1. Typical time-of-flight mass spectrum of the ions produced in the ion-trap experiment.



Fig. S2. UB3PW91/aug-cc-pvdz minimum-energy structures and relative free energies (in kJ/mol) at 70 K of the lowest energy $[Ti_2O_4D_2]^-$ isomers.



Fig. S3. Energetically low-lying UB3PW91/aug-cc-pvdz minimum-energy structures and relative free energies (in kJ/mol) at 70 K of $Ti_2O_4^-$.



Fig. S4. Evolution of the orbital energies during D_2 dissociation on the neutral Ti_2O_4 (a) and anionic trans- $Ti_2O_4^-$ (b) clusters. The important molecular orbitals are shown as inserts.

Evolution of the orbital energies during dissociation of D_2 molecule on the neutral Ti_2O_4 and anionic trans- $Ti_2O_4^$ clusters is shown in Fig. S4a and S4b, respectively. Here, the orbital energies for anionic clusters were taken from those of α -spin orbitals determined by solving the spin-unrestricted Kohn-Sham equations. Fig. S4a demonstrates considerable rearrangement of the electronic structure of the neutral $[Ti_2O_4D_2]$ system during D₂ dissociation. One can see that the HOMO of the neutral $Ti_2O_4D_2$ system is stabilized, while HOMO-1 is destabilized along the D_2 dissociation pathway, resulting in the crossing of HOMO and HOMO-1 before the transition state TS^{0} . While orbital character of the original HOMO remains basically unchanged along the dissociation pathway (although O-2p orbital at the terminal O atom disappears after the O-D bond formation), the original HOMO-1 undergoes considerable change forming a Ti-D bonding orbital between D-1s and Ti- $3d_z^2$. In the final configuration \mathbf{P}^0 the Ti-D bonding orbital of D-1s and Ti- $3d_z^2$ dominates HOMO for the whole system. MO destabilization is responsible for the formation of the energy barrier for D_2 dissociation. In the anionic $[Ti_2O_4D_2]^-$ system evolution of the electronic structure during D₂ dissociation is considerably different. Neither HOMO nor HOMO-1 change their character and participate in the interaction with D₂. Fig. S4b demonstrates that the orbital which is destabilized during D₂ dissociation and changes its order with HOMO-3 is the energetically low-lying HOMO-5. This orbital undergoes the strong change in its character similar to HOMO-1 in the neutral system. Such differences in the electronic structure of neutral and anionic species driven by the charge excess can be responsible for lowering of the activation barrier for the dissociative adsorption of D_2 on Ti_2O_4 .

Mode	R _{cis}	R _{trans}	I _{cis}	Itrans	P ₁	P ₂	P ₃	P ₄	P 5
ν(D-D)			2703(75)	2722(85)					
v(O-D)					2877(53)	2836(38)	2817(24)	2855(59)	2857(47)
v(Ti-D)					1086(340)	1027(241)	1031(222)	1130(263)	1138(351)
v(Ti-O)	987(244)	964(95)	962(250)	950(125)	997(325)	990(499)	996(523)	951(455)	951(415)
	949(785)	935(1002)	921(806)	921(844)					
VS,1			747(193)	753(230)	779(485)	792(239)	794(240)	569(299)	570(333)
VAS,1			726(201)	728(198)	727(227)	741(243)	741(243)	454(2)	456(2)
VS,2			550(261)	556(343)	634(416)	601(122)	595(147)	818(418)	816(405)
v(Ti-OD)					610(13)	647(417)	647(417)	662(279)	658(227)
δ(ring)	712(173)	721(211)							
δ(Ti-OD)						464(63)	446(27)		
VAS,2			451(3)	447(3)	449(25)	430(16)	423(4)	746(248)	745(237)
δ(Ti-D)					420(14)			407(29)	405(30)

Table S1. UB3PW91/aug-cc-pvdz harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol) of Ti₂O₄ and Ti₂O₄D₂⁻.