Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Computational study of ethanol adsorption and reaction over rutile TiO_2 (110) surface.

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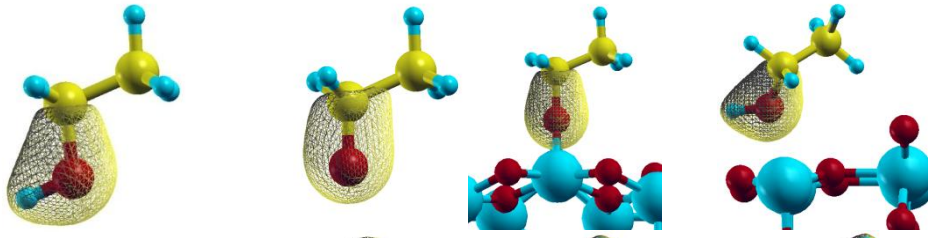
Ethoxide	Dissociative Adsorption	Ethoxide Difference	Ethanol Gas Difference	Dissociative Adsorption Difference	Ethanol Gas	Ethoxide	Dissociated Adsorption
-18.8	-19.6				O8 2s	O8 2s, C7 2s	O8 2s, C7 2s
-12.9	-12.7	5.9	6.9	6.4	C2 2s, C7 2s	C2 2s C7 $2p_z$	C2 2s, C7 2s
-9.3	-9.1	9.5	10.5	9.8	C7 2s, C2 2s	C7 2s, C2 $2p_y$, H3, H6, C7 $2p_z$, O8 2s	C7 2s, C2 2s, O8 2pz, C7 2py, C2 2py, H3, H6
-6.0	-6.7	12.8	12.9	13.1	O8 $2p_x$, C7 $2p_y$, O8 $2p_z$	C7 $2p_x$, C2 $2p_x$	O8 2pz, C7 2px
-5.4	-5.4	13.4	14.2	13.4	C7 $2p_z$, C7 $2p_y$ C2 $2p_z$, C2 $2p_x$	C7 2px, C 7 $2p_y$, H1, C2 $2p_y$, O8 $2p_x$	C7 $2p_x$, H3, C7 $2p_z$, O8 $2p_x$
-4.4	-3.9	14.4	15.7	14.5	O8 $2p_y$, C7 $2p_z$, C2 $2p_x$, C2 $2p_y$	C2 $2p_y$, C7 $2p_y$, O8 $2p_y$	O8 $2p_y$, C7 $2p_y$, C7 $2p_y$
-3.7	-3.4	15.2	16.2	15.6	C2 $2p_y$, C2 $2p_z$, H1	C7 $2p_x$, C2 $2p_x$, H6, H3, H5, H4 O2 $2p_x$	C2 $2p_z$, H1, C2 $2p_y$, H4, H5
-3.6	-2.8	15.2	16.8	15.8	C2 $2p_z$, C2 $2p_x$, H4, H5	O8 $2p_z$, C7 $2p_z$, O8 2s	C7 $2p_x$, O8 $2p_x$
-0.2	-2.1	18.7	17.5	17.7	O2 $2p_y$ O2 $2p_x$, C7 $2p_y$	O8 $2p_y$	O8 $2p_x$ (small O2p_y)
-0.1	-0.4	18.7	19.2	18.2	O8 $2p_z$,O8 $2p_x$	O8 $2p_x$	O8 $2p_y$, O8 $2p_x$

Table S1
Comparison of the orbitals of isolated ethanol and ethoxide (in the middle of the vacuum layer with a TiO_2 slab) and dissociatively adsorbed parallel ethanol. The difference columns list the energy difference between the current orbital and orbital 1 in eV. The makeup of orbitals lists the major components of the orbitals as determined by LDOS. The energetic separation and makeup of ethanol gas is somewhat between a gas and ethoxide structure though energetic separation is closer to an ethanol gas phase structure.

1)



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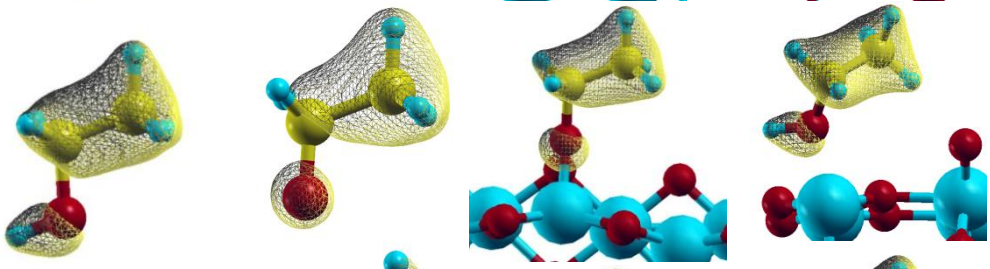

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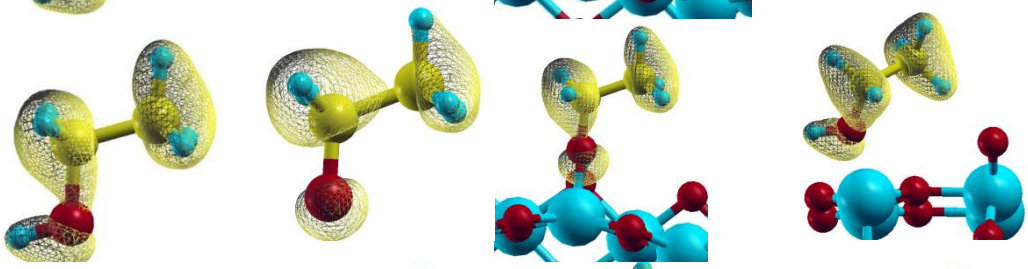

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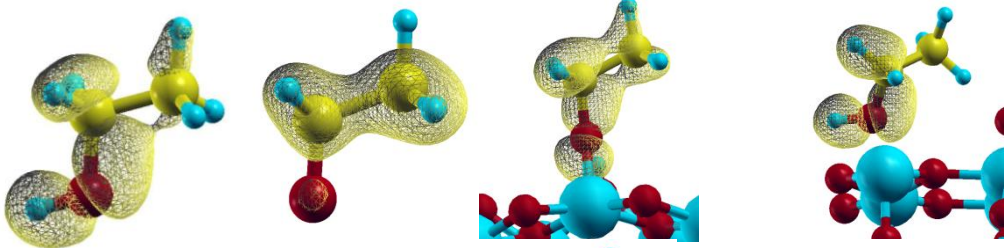

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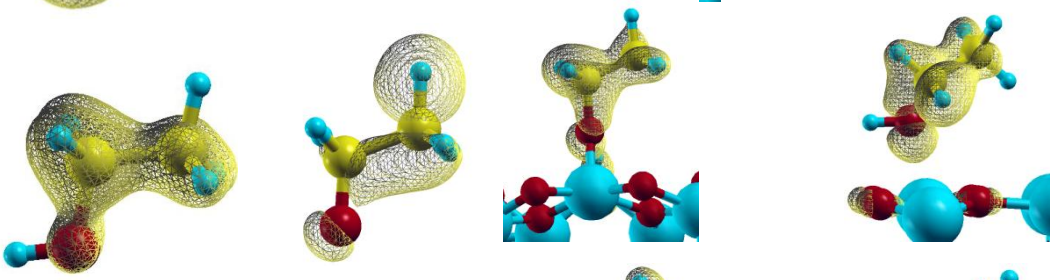

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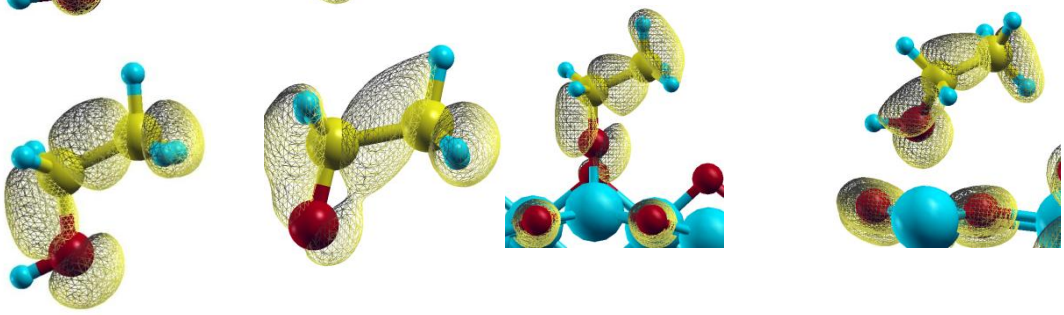

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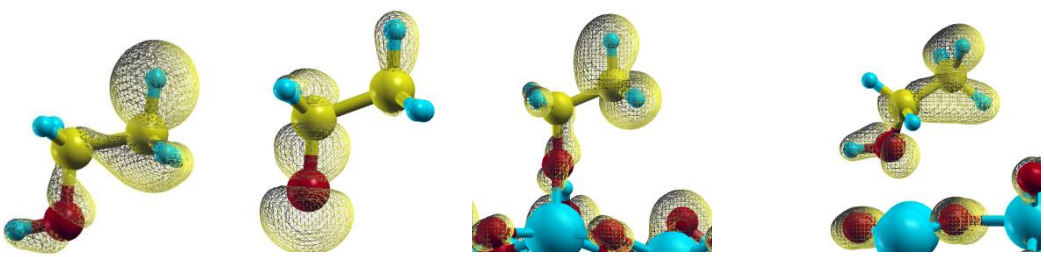

8)

9)

10)

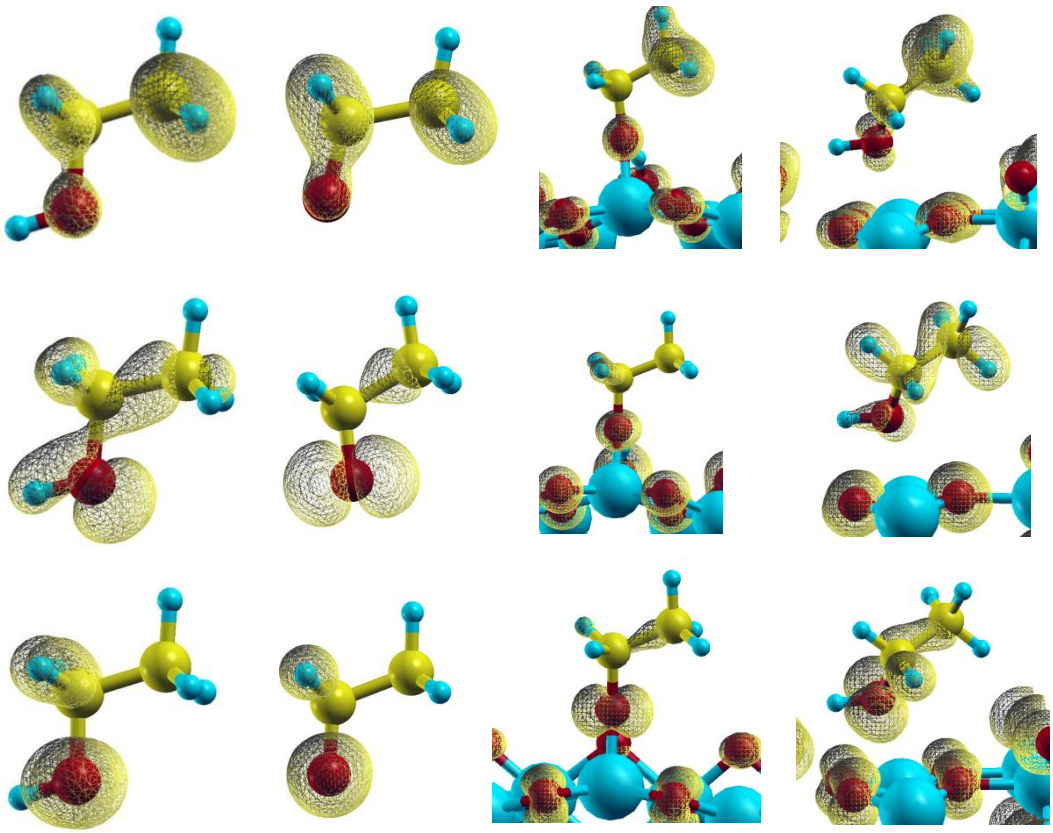

Figure S1
3D images of the integrated LDOS of ethanol, ethoxide, adsorbed ethoxide and ethanol as determined in Figures 8 and 9. All images are at 0.01 states/bohr^3. Orbitals numbers refer to tables 3 and 4. For ethanol gas imaging the Cs configuration is used as it compares best with the adsorbed molecular configuration.

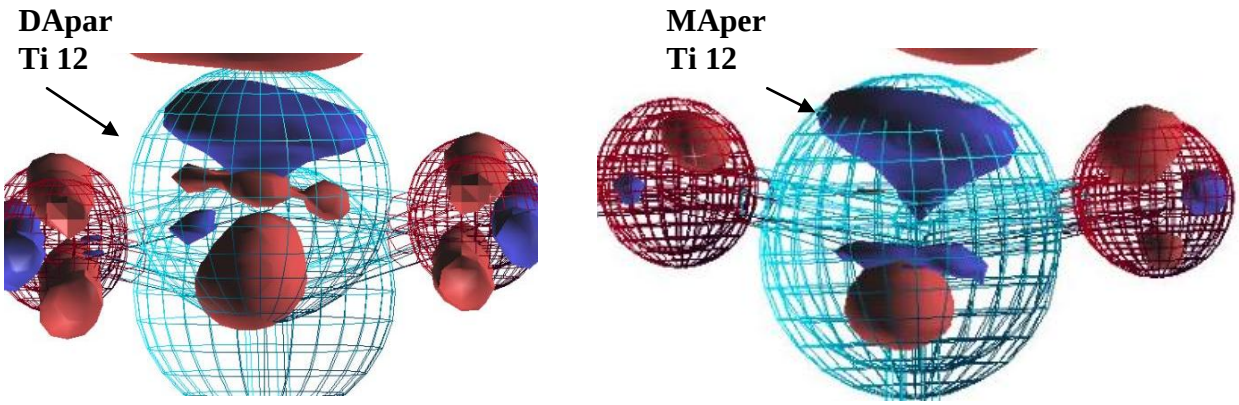

Figure S2
Close up of the Ti12 charge density difference with red as increased charge density and blue as decreased charge density.
Left) Dissociative parallel 0.008 e/bohr^3;
Right) Molecular Perpendicular 0.004 e/bohr^3.
Red is increase, blue is decrease in charge density.

		WF decrease (eV)	Refs
A) Oxygenates on TiO_2 (110)			
Experimental			
Water	Perfect	1.1, 1.2	(52, 64)
	Reduced	0.6, 0.9	(52, 65)
Formic Acid	Perfect	0.8	(66)
Pivalic Acid	Perfect	0.8	(67)
Methanol	Perfect	1.2	(68)
Theoretical			
Formaldehyde	Perfect/Reduced	0.5	(47)
Methanol	Perfect	1.6-2.7	(22)
Ethanol (molecular)	Perfect	0.55	This work
Ethanol (dissociative)	Perfect	0.28	This work
B) Ethanol on Metals			
Ag (110)	Experimental.	1.1	(69)
Mo_2C/Mo (110)	Experimental.	1.2	(70)
Rh (111)	Theoretical	2.7	(71)

Table S2

Literature decrease in work function of
A) TiO_2 with adsorbed oxygenates and B) Various metals with adsorbed ethanol.