Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information of:

Structure-Activity Relationships on Metal-Oxides: Alcohol Dehydration

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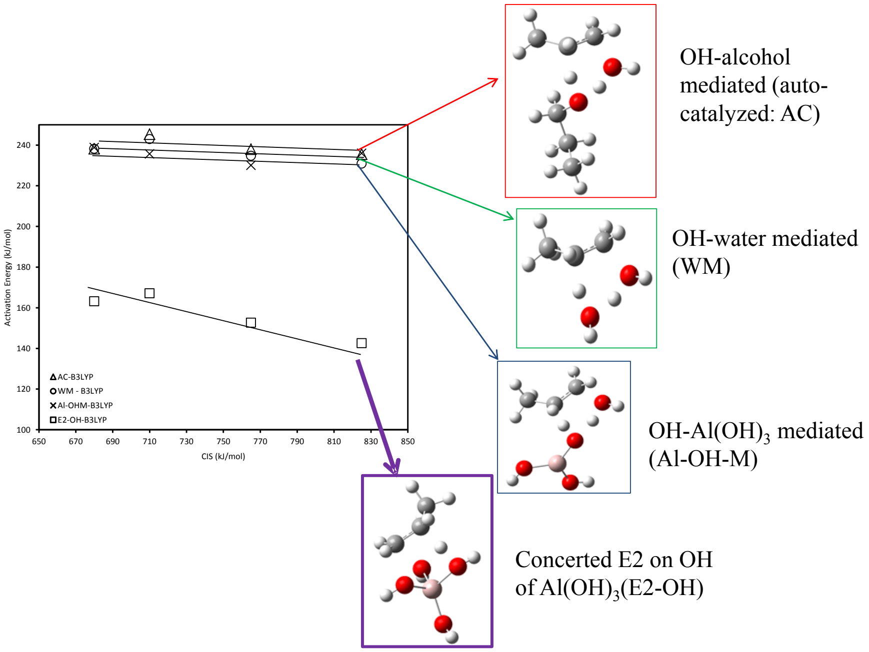

Figure 1S. DFT calculated dehydration barriers of OH-mediated mechanisms for the elimination of beta hydrogens of the alcohols involving another alcohol molecule (red), a water molecule (green), an Al(OH)$_3$ molecule (blue) and the E2 dehydration mechanism on an Al(OH)$_3$ molecule. The upper three mechanisms involve beta hydrogen transfer to the OH group of the alcohol through hydrogen bonds. These mechanisms show high barriers and there is no dependence on the type of the alcohol (CIS). The preferred dehydration mechanism is the concerted E2.

Table 1S: Calculated dehydration barriers with B3LYP and M062X functionals (basis set: 6-311G*). Values are in kJ/mol (electronic energies).

Alcohol	Al_2O_3: E2 on OH		Al_2O_3: E2 on O		TiO_2: E2 on OH		TiO_2: E2 on O		ZrO_2: E2 on OH		ZrO_2: E2 on O	
	B3LYP	M062X	B3LYP	M062X	B3LYP	M062X	B3LYP	M062X	B3LYP	M062X	B3LYP	M062X
Ethanol	159.81	185.94	132.02	157.09	189.57	214.71	188.64	212.26	177.68	204.42	173.17	195.13
1-Propanol	163.46	194.92	135.91	166.92	194.46	223.08	191.80	218.38	183.97	211.89	179.10	202.25
2-Propanol	150.62	178.21	125.51	162.24	184.78	213.84	180.92	207.35	175.25	201.67	170.16	191.77
t-Butanol	140.13	167.45	119.31	154.75	170.70	204.87	165.77	195.77	165.96	199.46	161.60	191.30

Table 2S: Natural Bond Orbital charge analysis of the formed carbenium ion on the transition state of 1-Propanol dehydration (concerted E2 mechanism) on the different oxides. Distances of C-OH, beta C-H bonds and H-C^1-C^2-C^3 dihedral angles were calculated (the angles of 1-Propanol transition state on TiO_2 involving O and OH are shown in purple on the right insets). The C-OH bond is significantly elongated than the beta C-H bond showing a charge splitting at the transition state and formation of a carbenium ion. The carbenium ion has sp2 character which is depicted on the H-C^1-C^2-C^3 dihedral angle change (from ~60^o on the initial state to almost planar on the transition state).

System	Total Carbenium Ion Charge (|e^-|)	C-OH (A)	C-H_β (A)	H-C^1-C^2-C^3 dihedral angles | ° |
TS: 1-Prop-Al_2O_3_OH	0.564	2.088	1.309	5.44
TS: 1-Prop-Al_2O_3_O	0.522	2.014	1.301	2.22
TS: 1-Prop-TiO_2_OH	0.538	2.004	1.318	5.48
TS: 1-Prop-TiO_2_O	0.582	2.039	1.305	5.00
TS: 1-Prop-ZrO_2_OH	0.516	2.012	1.335	4.45
TS: 1-Prop-ZrO_2_O	0.535	1.994	1.329	3.86
1-prop_gas_phase	-	1.425	1.095	58.98
1-prop_Al_adsorbed	-	1.462	1.094	58.80
1-prop_Ti_adsorbed	-	1.452	1.094	55.26
1-prop_Zr_adsorbed	-	1.450	1.094	57.60

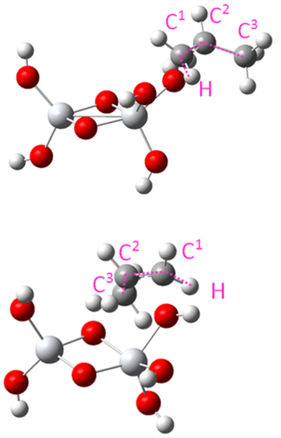

Table 3S: Binding Energies (BE) of alcohols on the different metal oxide clusters and Proton Affinities (PA) of the basic O and OH sites (all values are in kJ/mol).

Cluster	Eth	1-Prop	2-Prop	t-But	PA_O	PA_OH
Alumina	-131.0	-133.5	-131.4	-136.2	-930.07	-776.65
Titania	-69.1	-73.0	-71.6	-69.9	-909.63	-882.33
Zirconia	-80.3	-84.6	-83.4	-84.1	-954.1	-897.75