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Supporting Information

Heterogenised catalysts for the H-transfer reduction reaction of aldehydes: Influence of solvent and solvation effects on reaction performances

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Table S1. General Amber force field parameters

Atom type	Mass	Ptype	Sigma (nm)	Epsilon (kJ/mol)
c3	12.010000	A	0.33996695	0.4577296
c	12.010000	A	0.33996695	0.359824
o	16.000000	A	0.29599219	0.87864
hc	1.008000	A	0.26495328	0.0656888
h4	1.008000	A	0.25105526	0.06276
oh	16.000000	A	0.30664734	0.8803136
h1	1.008000	A	0.2471353	0.0656888
ho	1.008000	A	0	0
Y1	16.000000	A	0.29599219	0.87864
Y2	16.000000	A	0.29599219	0.87864
Y3	16.000000	A	0.29599219	0.87864
M1	26.980000	A	0.22272468	0.010193772
os	16.000000	A	0.30000123	0.71128
ca	12.010000	A	0.33996695	0.359824
ha	1.008000	A	0.25996425	0.06276

Table S2. Parameters for cyclohexane

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
c3	C1	-0.380	1.220	-0.660	-0.07473300
hc	H2	-1.460	1.200	-0.440	0.03770000
hc	H3	-0.200	2.140	-1.220	0.03770000
c3	C4	0.380	1.220	0.660	-0.07473300
hc	H5	1.460	1.200	0.440	0.03770000
hc	H6	0.200	2.140	1.220	0.03770000
c3	C7	0.000	0.000	1.520	-0.07473300
hc	H8	0.840	-0.260	2.180	0.03770000
hc	H9	-0.840	0.260	2.180	0.03770000
c3	C10	-0.380	-1.220	0.660	-0.07473300
hc	H11	-0.200	-2.140	1.220	0.03770000
hc	H12	-1.460	-1.200	0.440	0.03770000
c3	C13	0.380	-1.220	-0.660	-0.07473300
hc	H14	0.200	-2.140	-1.220	0.03770000
hc	H15	1.460	-1.200	-0.440	0.03770000
c3	C16	0.000	0.000	-1.520	-0.07473300
hc	H17	0.840	0.260	-2.180	0.03770000
hc	H18	-0.840	-0.260	-2.180	0.033698

Table S3. Parameters for diethyl ether

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
os	O1	0.000	0.000	0.260	-0.4276000
c3	C2	0.000	1.180	-0.520	0.13040000
h1	H3	0.890	1.200	-1.170	0.02270000
h1	H4	-0.890	1.200	-1.170	0.02270000
c3	C5	0.000	2.380	0.410	-0.09610000
hc	H6	0.880	2.370	1.050	0.04470000
hc	H7	0.000	3.310	-0.160	0.04470000
hc	H8	-0.880	2.370	1.050	0.04470000
c3	C9	0.000	-1.180	-0.520	0.13040000
h1	H10	0.890	-1.200	-1.170	0.02270000
h1	H11	-0.890	-1.200	-1.170	0.02270000
c3	C12	0.000	-2.380	0.410	-0.09610000
hc	H13	-0.880	-2.370	1.050	0.04470000
hc	H14	0.000	-3.310	-0.160	0.04470000
hc	H15	0.880	-2.370	1.050	0.04470000

Table S4. Parameters for 1,4-dioxane

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
c3	C1	0.230	0.730	1.170	0.09140000
h1	H2	1.320	0.770	1.220	0.05720000
h1	H3	-0.190	1.260	2.020	0.05720000
c3	C4	-0.230	-0.730	1.170	0.09140000
h1	H5	0.190	-1.260	2.020	0.05720000
h1	H6	-1.320	-0.770	1.220	0.05720000
c3	C7	-0.230	-0.730	-1.170	0.09140000
h1	H8	0.190	-1.260	-2.020	0.05720000
h1	H9	-1.320	-0.770	-1.220	0.05720000
c3	C10	0.230	0.730	-1.170	0.09140000
h1	H11	1.320	0.770	-1.220	0.05720000
h1	H12	-0.190	1.260	-2.020	0.05720000
os	O13	-0.230	1.400	0.000	-0.41160000
os	O14	0.230	-1.400	0.000	-0.41160000

Table S5. Parameters for *n*-hexane

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
c3	C1	1.410	2.890	0.000	-0.09310000
hc	H2	0.900	3.280	0.880	0.03270000
hc	H3	0.900	3.280	-0.880	0.03270000
hc	H4	2.430	3.290	0.000	0.03270000
c3	C5	1.410	1.360	0.000	-0.08040000
hc	H6	1.960	1.000	-0.880	0.03870000
hc	H7	1.960	1.000	0.880	0.03870000
c3	C8	0.010	0.760	0.000	-0.07940000
hc	H9	-0.540	1.130	-0.880	0.03870000
hc	H10	-0.540	1.130	0.880	0.03870000
c3	C11	-0.010	-0.760	0.000	-0.07940000
hc	H12	0.540	-1.130	0.880	0.03870000
hc	H13	0.540	-1.130	-0.880	0.03870000
c3	C14	-1.410	-1.360	0.000	-0.08040000
hc	H15	-1.960	-1.000	-0.880	0.03870000
hc	H16	-1.960	-1.000	0.880	0.03870000
c3	C17	-1.410	-2.890	0.000	-0.09310000
hc	H18	-0.900	-3.280	0.880	0.03270000
hc	H19	-2.430	-3.290	0.000	0.03270000
hc	H20	-0.900	-3.280	-0.880	0.03270000

Table S6. Parameters for toluene

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
ca	C1	-0.000	0.910	0.000	-0.07730000
ca	C2	-0.010	0.190	1.200	-0.13100000
ca	C3	-0.010	-1.200	1.200	-0.12700000
ca	C4	-0.010	-1.900	0.000	-0.13500000
ca	C5	-0.010	-1.200	-1.200	-0.12700000
ca	C6	-0.010	0.190	-1.200	-0.13100000
ha	H7	-0.010	0.730	2.140	0.13000200
ha	H8	-0.010	-1.730	2.140	0.13000200
ha	H9	-0.010	-2.980	0.000	0.13000200
ha	H10	-0.010	-1.730	-2.140	0.13000200
ha	H11	-0.010	0.730	-2.140	0.13000200
c3	C12	0.030	2.420	0.000	-0.05380000
hc	H13	-0.460	2.820	0.880	0.04403000
hc	H14	1.060	2.780	0.000	0.04403000
hc	H15	-0.460	2.820	-0.880	0.04403000

Table S7. Parameters for 2-propanol

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
c3	C1	-1.327	-0.532	-0.090	-0.11160000
c3	C2	-0.002	0.042	0.367	0.13910000
c3	C3	1.177	-0.793	-0.102	-0.11160000
hc	H4	-2.149	0.101	0.243	0.04336700
hc	H5	-1.350	-0.582	-1.180	0.04336700
hc	H6	-1.470	-1.536	0.311	0.04336700
oh	O7	0.067	1.361	-0.162	-0.60180000
h1	H8	0.006	0.090	1.464	0.02870000
hc	H9	2.123	-0.355	0.224	0.04336700
hc	H10	1.122	-1.806	0.299	0.04336700
hc	H11	1.181	-0.848	-1.192	0.04336700
ho	H12	0.915	1.746	0.076	0.39699800

Table S8. Parameters for propionaldehyde

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
c3	C1	-1.669	-0.296	-0.174	-0.09210000
c3	C2	-0.472	0.603	0.136	-0.20440000
c	C3	0.778	-0.213	0.315	0.56490000
o	O4	1.794	-0.055	-0.301	-0.52810000
hc	H5	-2.585	0.290	-0.234	0.04003300
hc	H6	-1.533	-0.812	-1.124	0.04003300
hc	H7	-1.805	-1.050	0.603	0.04003300
hc	H8	-0.298	1.338	-0.649	0.07320050
hc	H9	-0.650	1.136	1.075	0.07320050
h4	H10	0.705	-1.020	1.075	-0.00680000

Table 9. Parameters for aluminium isopropoxide

Atom type	Atom name	Coordination			Charge
		X	Y	Z	
SB1					
Y1	O	1.332	-1.026	0.122	-0.82502400
c3	C	2.716	-0.788	0.297	0.61194600
c3	C1	3.405	-2.126	0.495	-0.27844500
c3	C2	3.277	-0.030	-0.896	-0.35086500
h1	H	2.858	-0.178	1.197	-0.07221900
hc	H1	4.473	-1.990	0.671	0.06113400
hc	H2	2.973	-2.652	1.346	0.06113400
hc	H3	3.272	-2.743	-0.395	0.06113400
hc	H4	4.344	0.159	-0.771	0.07473300
hc	H5	3.133	-0.618	-1.805	0.07473300
hc	H6	2.769	0.929	-1.011	0.07473300
SB2					
Y2	O	0.239	1.658	-0.085	-0.82607800
c3	C	-0.644	2.760	-0.166	0.62039300
c3	C1	0.176	4.034	-0.073	-0.27291500
c3	C2	-1.695	2.679	0.930	-0.34389700
h1	H	-1.151	2.735	-1.138	-0.07719900
hc	H1	-0.461	4.914	-0.169	0.05848000
hc	H2	0.685	4.073	0.892	0.05848000
hc	H3	0.929	4.058	-0.860	0.05848000
hc	H4	-2.382	3.525	0.876	0.07267000
hc	H5	-2.274	1.759	0.836	0.07267000
hc	H6	-1.207	2.691	1.908	0.07267000
SB3					
Y3	O	-1.516	-0.641	-0.375	-0.82874400
c3	C	-2.058	-1.946	-0.428	0.61098700
c3	C1	-3.563	-1.829	-0.587	-0.27396400
c3	C2	-1.678	-2.732	0.817	-0.33227600
h1	H	-1.648	-2.460	-1.305	-0.07271000
hc	H1	-4.022	-2.814	-0.675	0.05938000
hc	H2	-3.986	-1.322	0.283	0.05938000
hc	H3	-3.805	-1.247	-1.476	0.05938000
hc	H4	-2.087	-3.742	0.780	0.07017400
hc	H5	-0.592	-2.802	0.909	0.07017400
hc	H6	-2.075	-2.231	1.703	0.07017400
AL1					
M1	AL	0.015	-0.007	-0.109	1.52129700

Table S10. T_1 and T_2 values of the solvents and reactants in SiO_2 and $Al(O^iPr)_3$-SiO_2

	SiO_2			$Al(O^iPr)_3$-SiO_2		
Compound	T_1 **(ms)**	T_2 **(ms)**	T_1/T_2	T_1 **(ms)**	T_2 **(ms)**	T_1/T_2
n-hexane	1446.01	198.31	7.3	755.26	276.21	2.7
cyclohexane	1382.35	181.42	7.6	540.23	168.71	3.2
toluene	2962.29	282.29	10.5	1767.61	438.61	4.0
1,4-dioxane	2187.9	192.31	11.4	203.96	38.41	5.3
diethyl ether	3217.54	282.29	11.4	961.34	122.76	7.8
propionaldehyde	600.19	120.55	5.0	144.73	57.23	2.5
2- propanol	1065.03	139.71	7.6	264.81	88.76	3.0

Table S11. T_1 and T_2 values of the solvents and reactants in TiO_2 and $Al(O^iPr)_3$-TiO_2

	TiO_2			$Al(O^iPr)_3$-TiO_2		
Compound	T_1 **(ms)**	T_2 **(ms)**	T_1/T_2	T_1 **(ms)**	T_2 **(ms)**	T_1/T_2
n-hexane	1683.06	200.01	8.4	711.02	243.66	2.9
cyclohexane	2301.59	232.5	9.9	647.82	176.17	3.7
toluene	2930.82	239.64	12.2	1890.64	454.21	4.2
1,4-dioxane	1894.64	153.85	12.3	185.37	34.57	5.4
diethyl ether	3601.48	286.28	12.6	954.95	119.47	8
propionaldehyde	800.24	156.69	5.1	177.29	77.87	2.3
2- propanol	988.85	111.77	8.9	262.94	88.67	3.0

Table S12. T_1 and T_2 values of the solvents and reactants in Al_2O_3 and $Al(O^iPr)_3$-Al_2O_3

	Al_2O_3			**$Al(O^iPr)_3$- Al_2O_3**		
Compound	**T_1 (ms)**	**T_2 (ms)**	**T_1/T_2**	**T_1 (ms)**	**T_2 (ms)**	**T_1/T_2**
n-hexane	1750.02	216.14	8.1	754.38	270.39	2.8
cyclohexane	1943.27	227.15	8.6	482.71	131.8	3.7
toluene	2797.52	235.69	11.9	1762.53	428.19	4.1
1,4-dioxane	1696.14	142.8	11.9	194.75	36.69	5.3
diethyl ether	2529.47	207.57	12.2	909.17	114.63	7.9
propionaldehyde	1287.14	248.00	5.2	177.27	57.82	3.0
2- propanol	1056.77	129.64	8.2	264.54	87.19	3.0

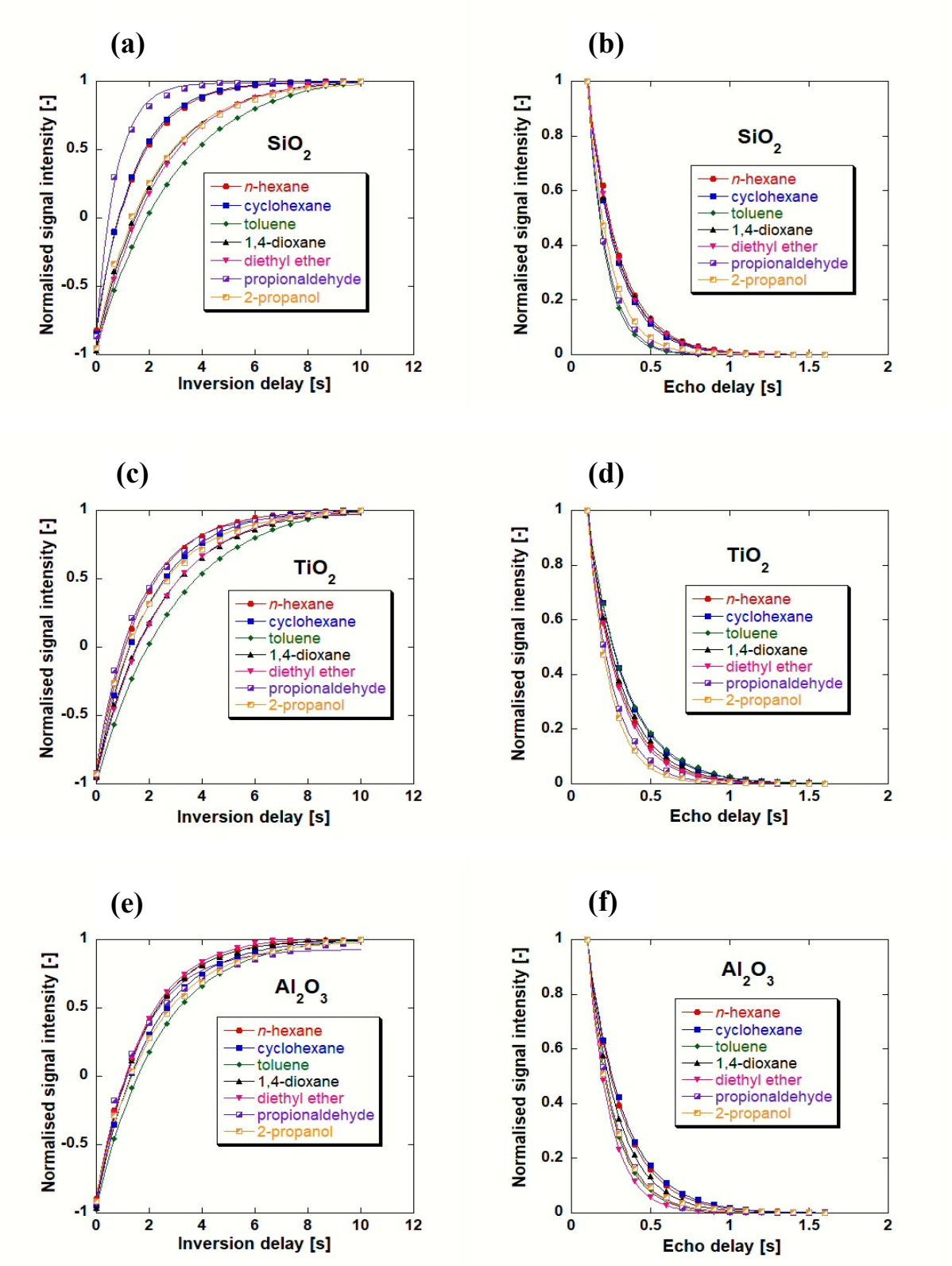

Figure S1. T_1 relaxation plots for solvents and reactants within (a) SiO_2, (c) TiO_2 and (e) γ-Al_2O_3. T_2 CPMG plots for solvents and reactants within (b) SiO_2, (d) TiO_2 and (f) γ- Al_2O_3.

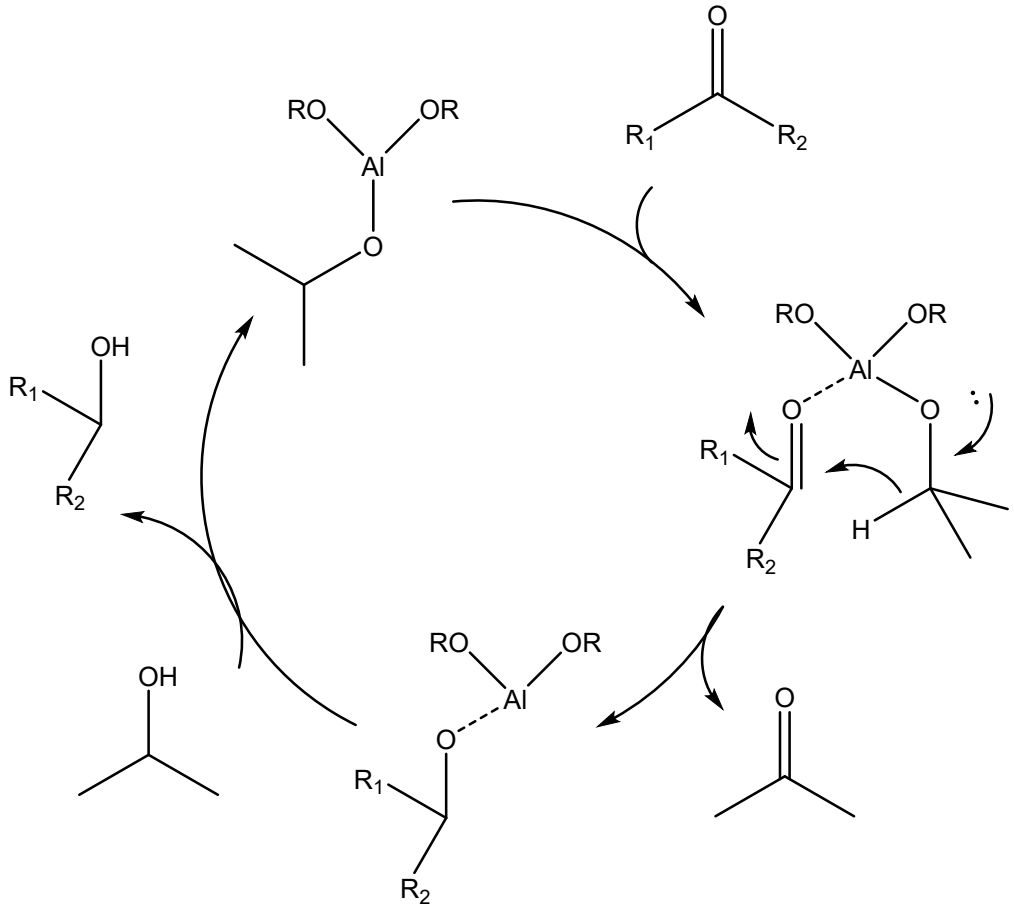

Figure S2. Mechanism of MPV reduction.