Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

for

Enhancement of Hydrogen Storage Capacity of $Mg(AlH_4)_2$ by Excess Electron: A DFT Study

Sunwoo Kang[a,b] *S. Karthikeyan*[a] *and Jin Yong Lee**[a]

[a]Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea

[b]Division of Materials Science, Korea Basic Science Institute (KBSI), Daejeon 305-333, Korea

Contents

Table S1. The Cartesian coordinates and NBO charge populations of DMA, DMA_1^-, H-DMA_1^-, 2H-DMA_1^-, DMA_2^-, H-DMA_2^-, 2H-DMA_2^-, TMA, TMA-, H-TMA^-, and 2H-TMA^-.

DMA				
	Charge	Cartesian coordinate		
Mg	1.03001	1.703333	-1.528445	0.000000
Al	0.96436	1.703333	1.198122	0.000000
H	-0.36010	1.738338	0.057973	1.205143
H	-0.45323	0.164012	1.750975	0.000000
Al	0.75252	3.283850	-3.429047	0.000000
H	-0.33773	2.156223	-3.118011	-1.192760
H	-0.33773	2.156223	-3.118011	1.192760
H	-0.29578	2.803993	2.319681	0.000000
H	-0.27463	4.205200	-4.697050	0.000000
H	-0.32758	3.814473	-1.864460	0.000000
H	-0.36010	1.738338	0.057973	-1.205143
Mg	1.03001	-1.703333	1.528445	0.000000
Al	0.96436	-1.703333	-1.198122	0.000000
H	-0.36010	-1.738338	-0.057973	1.205143
H	-0.45323	-0.164012	-1.750975	0.000000
Al	0.75252	-3.283850	3.429047	0.000000
H	-0.33773	-2.156223	3.118011	-1.192760
H	-0.33773	-2.156223	3.118011	1.192760
H	-0.36010	-1.738338	-0.057973	-1.205143
H	-0.32758	-3.814473	1.864460	0.000000
H	-0.29578	-2.803993	-2.319681	0.000000
H	-0.27463	-4.205200	4.697050	0.000000

DMA_1^-				
	Charge	Cartesian coordinate		
Mg	0.87120	0.000000	0.000000	-1.611672
Mg	0.87168	0.000000	0.000000	1.619372
Al	0.77646	-2.489397	0.032920	-2.781532
H	-0.40078	1.211197	-1.130733	-2.637044
H	-0.39110	1.629811	1.113387	-1.904621
Al	0.77646	2.489397	-0.032920	-2.781532
H	-0.40078	-1.211197	1.130733	-2.637044
H	-0.33599	2.662498	0.411952	-4.304498
Al	0.77547	0.000000	-2.495130	2.778580
H	-0.40082	1.121085	1.239830	2.619856
H	-0.39079	-1.145768	1.606124	1.930784
Al	0.77547	0.000000	2.495130	2.778580
H	-0.39079	1.145768	-1.606124	1.930784

H	-0.40082	-1.121085	-1.239830	2.619856
H	-0.33407	-3.748344	0.554028	-1.954555
H	-0.33599	-2.662498	-0.411952	-4.304498
H	-0.39110	-1.629811	-1.113387	-1.904621
H	-0.33407	3.748344	-0.554028	-1.954555
H	-0.33381	-0.477589	-3.759068	1.933120
H	-0.33601	0.417825	-2.669435	4.309133
H	-0.33381	0.477589	3.759068	1.933120
H	-0.33601	-0.417825	2.669435	4.309133

$H\text{-}DMA_1^-$

	Charge	Cartesian coordinate		
Mg	1.10893	0.000000	0.000000	1.791249
Mg	1.10893	0.000000	0.000000	-1.791249
Al	0.77734	-1.776482	1.777752	2.905787
H	-0.38409	-1.856447	0.163822	2.436179
H	-0.38387	-0.165503	1.860916	2.428204
Al	0.77734	1.776482	-1.777752	2.905787
H	-0.38409	1.856447	-0.163822	2.436179
H	-0.33720	1.893284	-1.901478	4.492130
Al	0.77734	1.776482	1.777752	-2.905787
H	-0.38387	0.165503	1.860916	-2.428204
H	-0.38409	1.856447	0.163822	-2.436179
Al	0.77734	-1.776482	-1.777752	-2.905787
H	-0.38409	-1.856447	-0.163822	-2.436179
H	-0.38387	-0.165503	-1.860916	-2.428204
H	-0.33193	-2.688844	2.680429	1.961424
H	-0.33720	-1.893284	1.901478	4.492130
H	-0.38387	0.165503	-1.860916	2.428204
H	-0.33193	2.688844	-2.680429	1.961424
H	-0.33193	2.688844	2.680429	-1.961424
H	-0.33720	1.893284	1.901478	-4.492130
H	-0.33193	-2.688844	-2.680429	-1.961424
H	-0.33720	-1.893284	-1.901478	-4.492130
H	-0.57883	0.000000	0.000000	0.000000

$2H\text{-}DMA_1^-$

	Charge	Cartesian coordinate		
Mg	1.01424	0.000000	0.000000	1.815443
Mg	1.01424	0.000000	0.000000	-1.815443
Al	0.79665	0.000000	2.451481	3.031429
H	-0.37965	1.086181	-1.158571	2.945974
H	-0.38023	-1.071049	-1.641104	2.017908
Al	0.79665	0.000000	-2.451481	3.031429
H	-0.37965	-1.086181	1.158571	2.945974

H	-0.33679	-0.605472	-2.556932	4.503278
Al	0.79665	0.000000	-2.451481	-3.031429
H	-0.37965	-1.086181	1.158571	-2.945974
H	-0.38023	1.071049	1.641104	-2.017908
Al	0.79665	0.000000	2.451481	-3.031429
H	-0.38023	-1.071049	-1.641104	-2.017908
H	-0.37965	1.086181	-1.158571	-2.945974
H	-0.33088	-0.616263	3.736413	2.323023
H	-0.33679	0.605472	2.556932	4.503278
H	-0.38023	1.071049	1.641104	2.017908
H	-0.33088	0.616263	-3.736413	2.323023
H	-0.33088	0.616263	-3.736413	-2.323023
H	-0.33679	-0.605472	-2.556932	-4.503278
H	-0.33088	-0.616263	3.736413	-2.323023
H	-0.33679	0.605472	2.556932	-4.503278
H	-0.25244	0.680956	-0.390108	0.000000
H	-0.25244	-0.680956	0.390108	0.000000

DMA_2^-

	Charge	Cartesian coordinate		
Mg	0.90829	0.000000	1.577567	-0.051426
Al	0.88849	-2.542894	0.000000	1.207992
H	-0.45025	-1.500469	1.296842	1.084014
H	-0.45025	-1.500469	-1.296842	1.084014
Al	0.75817	0.000000	4.105593	-1.185406
H	-0.39346	0.000000	2.526093	-1.780870
H	-0.33653	1.381194	4.827834	-1.531108
H	-0.34529	-3.179553	0.000000	2.675921
H	-0.33653	-1.381194	4.827834	-1.531108
H	-0.39706	0.000000	3.536175	0.388501
H	-0.34559	-3.506236	0.000000	-0.065870
Mg	0.90829	0.000000	-1.577567	-0.051426
Al	0.88849	2.542894	0.000000	1.207992
H	-0.45025	1.500469	-1.296842	1.084014
H	-0.45025	1.500469	1.296842	1.084014
Al	0.75817	0.000000	-4.105593	-1.185406
H	-0.39346	0.000000	-2.526093	-1.780870
H	-0.33653	-1.381194	-4.827834	-1.531108
H	-0.34559	3.506236	0.000000	-0.065870
H	-0.39706	0.000000	-3.536175	0.388501
H	-0.34529	3.179553	0.000000	2.675921
H	-0.33653	1.381194	-4.827834	-1.531108

$H\text{-}DMA_2^-$

	Charge	Cartesian coordinate		
Mg	1.10893	0.000000	0.000000	1.791249

Mg	1.10893	0.000000	0.000000	-1.791249
Al	0.77734	-1.776482	1.777752	2.905787
H	-0.38409	-1.856447	0.163822	2.436179
H	-0.38387	-0.165503	1.860916	2.428204
Al	0.77734	1.776482	-1.777752	2.905787
H	-0.38409	1.856447	-0.163822	2.436179
H	-0.33720	1.893284	-1.901478	4.492130
Al	0.77734	1.776482	1.777752	-2.905787
H	-0.38387	0.165503	1.860916	-2.428204
H	-0.38409	1.856447	0.163822	-2.436179
Al	0.77734	-1.776482	-1.777752	-2.905787
H	-0.38409	-1.856447	-0.163822	-2.436179
H	-0.38387	-0.165503	-1.860916	-2.428204
H	-0.33193	-2.688844	2.680429	1.961424
H	-0.33720	-1.893284	1.901478	4.492130
H	-0.38387	0.165503	-1.860916	2.428204
H	-0.33193	2.688844	-2.680429	1.961424
H	-0.33193	2.688844	2.680429	-1.961424
H	-0.33720	1.893284	1.901478	-4.492130
H	-0.33193	-2.688844	-2.680429	-1.961424
H	-0.33720	-1.893284	-1.901478	-4.492130
H	-0.57883	0.000000	0.000000	0.000000

$2H\text{-}DMA_2^-$

	Charge	Cartesian coordinate		
Mg	1.10754	0.000000	1.625509	0.128619
Al	0.92874	2.545174	0.000000	-1.131057
H	-0.45069	1.507670	1.291767	-0.957609
H	-0.45069	1.507670	-1.291767	-0.957609
Al	0.76609	0.000000	4.247385	1.018473
H	-0.38529	0.000000	2.729823	1.751198
H	-0.33716	-1.380591	4.993990	1.311245
H	-0.34810	3.106331	0.000000	-2.625600
H	-0.33716	1.380591	4.993990	1.311245
H	-0.37995	0.000000	3.549833	-0.498381
H	-0.34755	3.567439	0.000000	0.095843
Mg	1.10754	0.000000	-1.625509	0.128619
Al	0.92874	-2.545174	0.000000	-1.131057
H	-0.45069	-1.507670	-1.291767	-0.957609
H	-0.45069	-1.507670	1.291767	-0.957609
Al	0.76609	0.000000	-4.247385	1.018473
H	-0.38529	0.000000	-2.729823	1.751198
H	-0.33716	1.380591	-4.993990	1.311245
H	-0.34755	-3.567439	0.000000	0.095843
H	-0.37995	0.000000	-3.549833	-0.498381
H	-0.34810	-3.106331	0.000000	-2.625600
H	-0.33716	-1.380591	-4.993990	1.311245

H	-0.53157	0.000000	0.000000	0.979638

TMA

	Charge	Cartesian coordinate		
Al	0.96674	0.000000	3.486377	0.000000
Al	0.75103	4.432899	5.577134	0.000000
H	-0.45703	-0.349271	1.892157	0.000000
H	-0.36217	1.128890	3.670031	1.204753
H	-0.29757	-1.242376	4.449951	0.000000
H	-0.36217	1.128890	3.670031	-1.204753
H	-0.33850	4.231712	4.422746	-1.192272
H	-0.32541	2.828283	5.961281	0.000000
H	-0.27513	5.615652	6.605795	0.000000
H	-0.33850	4.231712	4.422746	1.192272
Al	0.97294	-2.706806	-0.387538	0.000000
Al	0.97294	2.706806	0.387538	0.000000
H	-0.45351	-3.111575	-1.970473	0.000000
H	-0.36374	-1.579229	-0.218746	1.205863
H	-0.29905	-3.929568	0.601654	0.000000
H	-0.36374	-1.579229	-0.218746	-1.205863
H	-0.36374	1.579229	0.218746	-1.205863
H	-0.45351	3.111575	1.970473	0.000000
H	-0.29905	3.929568	-0.601654	0.000000
H	-0.36374	1.579229	0.218746	1.205863
Al	0.75103	-4.432899	-5.577134	0.000000
Al	0.96674	0.000000	-3.486377	0.000000
H	-0.32541	-2.828283	-5.961281	0.000000
H	-0.33850	-4.231712	-4.422746	1.192272
H	-0.27513	-5.615652	-6.605795	0.000000
H	-0.33850	-4.231712	-4.422746	-1.192272
H	-0.36217	-1.128890	-3.670031	-1.204753
H	-0.45703	0.349271	-1.892157	0.000000
H	-0.29757	1.242376	-4.449951	0.000000
H	-0.36217	-1.128890	-3.670031	1.204753
Mg	1.03066	2.703118	3.809009	0.000000
Mg	1.03029	0.000000	0.000000	0.000000
Mg	1.03066	-2.703118	-3.809009	0.000000

TMA^-

	Charge	Cartesian coordinate		
Mg	0.94235	0.000000	1.800285	-0.124989
Mg	0.94235	-1.559092	-0.900142	-0.124989
Al	0.95250	-2.595704	1.689068	-2.027832
H	-0.46155	-1.387069	2.474830	-1.157570
H	-0.46250	-2.585937	0.185003	-1.304213
Al	0.90869	-2.697368	0.417161	2.132076
H	-0.41928	-2.864073	-1.014960	1.247727
H	-0.33284	-3.949865	1.360345	1.874314

Al	0.90869	1.709956	2.127409	2.132076
H	-0.45017	1.474659	0.769994	1.121751
H	-0.41928	0.553055	2.987840	1.247727
Al	0.95250	2.760628	1.403412	-2.027832
H	-0.46155	2.836800	-0.036178	-1.157570
H	-0.46250	1.453186	2.146986	-1.304213
Al	0.90869	0.987412	-2.544570	2.132076
H	-0.45017	-0.070495	-1.662089	1.121751
H	-0.41928	2.311018	-1.972880	1.247727
Al	0.95250	-0.164924	-3.092480	-2.027832
H	-0.46155	-1.449731	-2.438652	-1.157570
H	-0.46250	1.132751	-2.331989	-1.304213
H	-0.34008	-2.105417	1.547955	-3.535267
H	-0.34212	-3.970803	2.424545	-1.698820
H	-0.45017	-1.404164	0.892095	1.121751
H	-0.32834	-2.188808	0.085399	3.596779
H	-0.32834	1.168362	1.852864	3.596779
H	-0.33284	3.153026	2.740511	1.874314
H	-0.34212	4.085119	2.226544	-1.698820
H	-0.34008	2.393277	1.049367	-3.535267
H	-0.32834	1.020446	-1.938263	3.596779
H	-0.33284	0.796839	-4.100856	1.874314
H	-0.34008	-0.287860	-2.597322	-3.535267
H	-0.34212	-0.114316	-4.651089	-1.698820
Mg	0.94235	1.559092	-0.900142	-0.124989

		H-TMA$^-$		
	Charge		Cartesian coordinate	
Mg	1.05604	-0.741447	1.651743	-0.145117
Mg	1.05592	-1.058736	-1.467987	-0.143014
Al	0.96881	-3.105155	0.450738	-2.004908
H	-0.45648	-2.278872	1.663155	-1.175269
H	-0.45621	-2.478646	-0.919103	-1.288000
Al	0.92434	-2.606626	-0.734493	2.132185
H	-0.40870	-2.177590	-2.108651	1.244664
H	-0.33349	-4.141077	-0.399674	1.892447
Al	0.92423	0.662593	2.624757	2.133095
H	-0.44324	1.041045	1.310356	1.127447
H	-0.40867	-0.739803	2.941016	1.242341
Al	0.96891	1.947231	2.462878	-2.002283
H	-0.45649	2.582433	1.141624	-1.170414
H	-0.45632	0.446942	2.605961	-1.287210
Al	0.92435	1.937461	-1.885207	2.137692
H	-0.44332	0.611808	-1.555497	1.129680
H	-0.40862	2.914551	-0.829662	1.248166
Al	0.96888	1.163620	-2.918521	-1.999302
H	-0.45644	-0.299567	-2.807541	-1.170173
H	-0.45630	2.036029	-1.689277	-1.284297

H	-0.34226	-2.644561	0.499273	-3.527990
H	-0.34462	-4.646961	0.588905	-1.632164
H	-0.44326	-1.656981	0.249021	1.125831
H	-0.32814	-1.990182	-0.829597	3.589419
H	-0.32809	0.268282	2.138293	3.589244
H	-0.33348	1.720707	3.785939	1.895984
H	-0.34464	2.837440	3.729315	-1.629788
H	-0.34225	1.760856	2.038235	-3.525166
H	-0.32807	1.710967	-1.299999	3.593236
H	-0.33348	2.413108	-3.382615	1.901657
H	-0.34223	0.892008	-2.546942	-3.523244
H	-0.34463	1.815193	-4.321982	-1.623765
Mg	1.05595	1.801314	-0.183928	-0.141826
H	-0.50802	0.000672	-0.000477	-0.737386

2H-TMA$^-$

	Charge	Cartesian coordinate		
Mg	1.16439	0.213999	-1.888515	0.003581
Mg	1.16437	-1.742501	0.758929	0.003581
Al	0.95608	-2.208891	-2.074455	2.038662
H	-0.46242	-0.814953	-2.692567	1.316633
H	-0.47840	-2.314788	-0.621083	1.232822
Al	0.95622	-2.590388	-1.412213	-2.109871
H	-0.45662	-2.828150	0.064812	-1.326259
H	-0.34117	-3.856995	-2.325967	-1.806579
Al	0.95616	2.518207	-1.537234	-2.109871
H	-0.47556	2.328584	-0.130335	-1.236547
H	-0.45661	1.357947	-2.481655	-1.326259
Al	0.95608	2.900976	-0.875728	2.038662
H	-0.46242	2.739309	0.640514	1.316633
H	-0.47840	1.695268	-1.694123	1.232822
Al	0.95619	0.072181	2.949448	-2.109871
H	-0.47556	-1.051419	2.081780	-1.236547
H	-0.45662	1.470203	2.416844	-1.326259
Al	0.95607	-0.692085	2.950183	2.038662
H	-0.46241	-1.924355	2.052054	1.316633
H	-0.47840	0.619520	2.315206	1.232822
H	-0.33983	-1.891941	-1.817352	3.577509
H	-0.34151	-3.423019	-3.015447	1.622350
H	-0.47556	-1.277164	-1.951446	-1.236547
H	-0.33809	-2.154806	-1.108409	-3.608435
H	-0.33808	2.037314	-1.311912	-3.608435
H	-0.34115	3.942844	-2.177272	-1.806579
H	-0.34151	4.322963	-1.456699	1.622350
H	-0.33983	2.519844	-0.729793	3.577509
H	-0.33809	0.117493	2.420322	-3.608435
H	-0.34116	-0.085849	4.503239	-1.806579
H	-0.33983	-0.627903	2.547145	3.577509

H	-0.34150	-0.899944	4.472145	1.622350
Mg	1.16440	1.528503	1.129585	0.003581
H	-0.56316	0.000000	0.000000	0.029032
H	0.03395	0.000000	0.000000	3.304686

Table S2. The calculated dissociation ΔH of MMA and MMA^- through $Mg(AlH_4)_2$ -> MgH_2 + 2Al + $3H_2$. The units are in $kJ/molH_2$.

	Calc.	Exp.
MMA	209.58	0
MMA^-	256.65	-

Complete Ref. 53:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.