Electronic Supplementary Material for PCCP

Supporting Information for

Multinuclear gallium-oxide cations in high-silica zeolites

Evgeny A. Pidko, Rutger A. van Santen and Emiel J.M. Hensen**

[a] *Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, NL-5600 MB Eindhoven, The Netherlands.*

** To whom correspondence should be addressed:*

e.a.pidko@tue.nl (E.A. Pidko)
e.j.m.hensen@tue.nl (E.J.M. Hensen)

Optimized structures and selected interatomic distances of various Ga_2O_2 isomers stabilized in mordenite models **I–III** are summarized in Figure S1. The corresponding experimental parameters and the molecular structure of complex **2** are shown for comparison.

Figure S2 shows the intermediates and the transition state structures involved in the elementary reactions of catalytic ethane dehydrogenation over $Ga_2O_2^{2+}$ binuclear site and those involved in the catalyst deactivation reaction path. Optimized structures for the respective reactions over partially hydrogenated $Ga(OH)(O)GaH^{2+}$ binuclear site and over the mononuclear GaO^+ ion are shown in Figures S3 and S4, respectively.

Selected optimized interatomic distances for the above structures are summarized in Tables S1, S2 and S3, respectively for the $Ga_2O_2^{2+}$, $Ga(OH)(O)GaH^{2+}$ and GaO^+ extra-framework sites in mordenite.

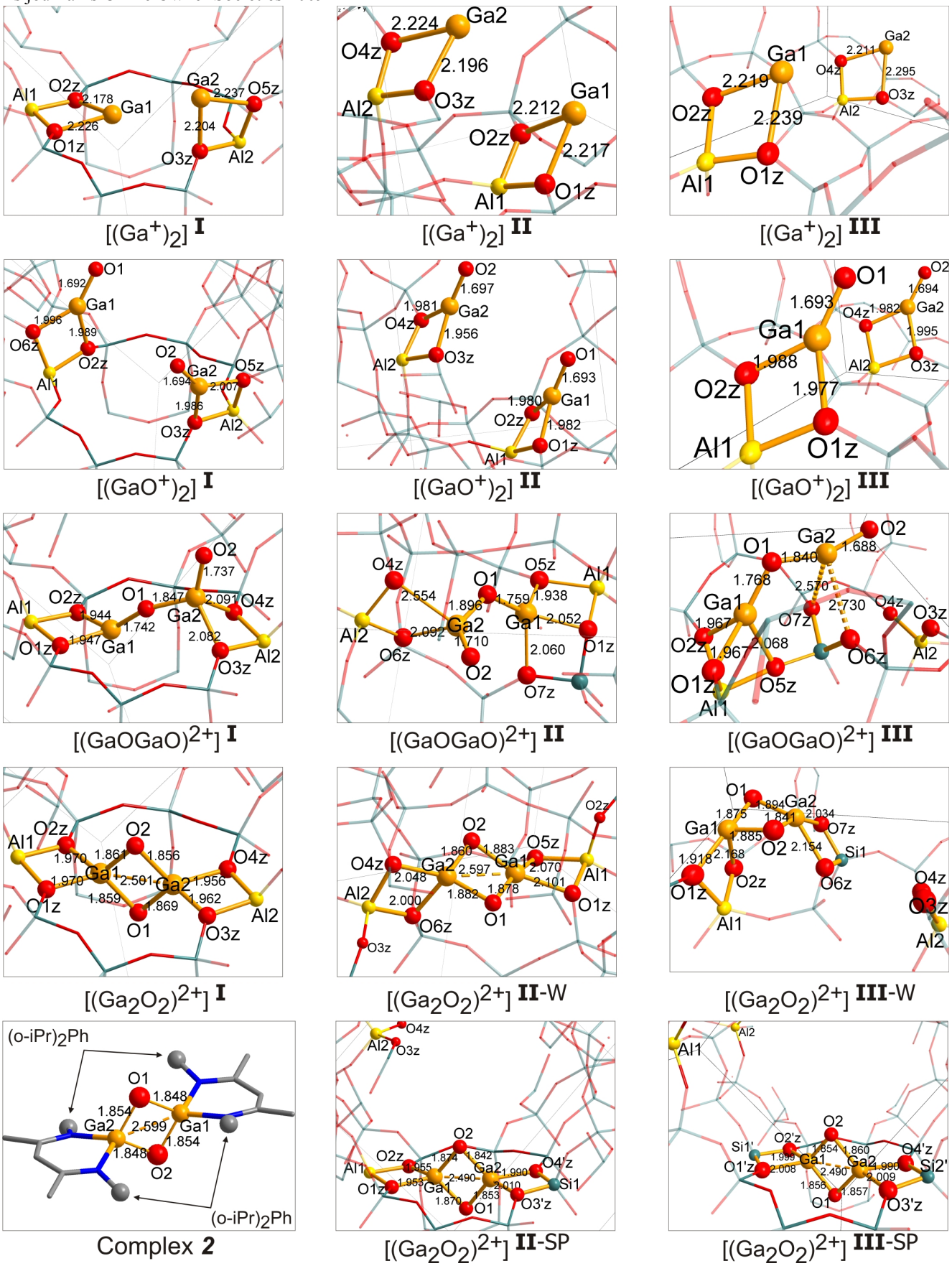

Figure S1. Optimized structures and selected interatomic distances (Å) of $(GaO)_2$ isomers stabilized in the mordenite models **I–III**. The respective data for ***2*** is provided for comparison.

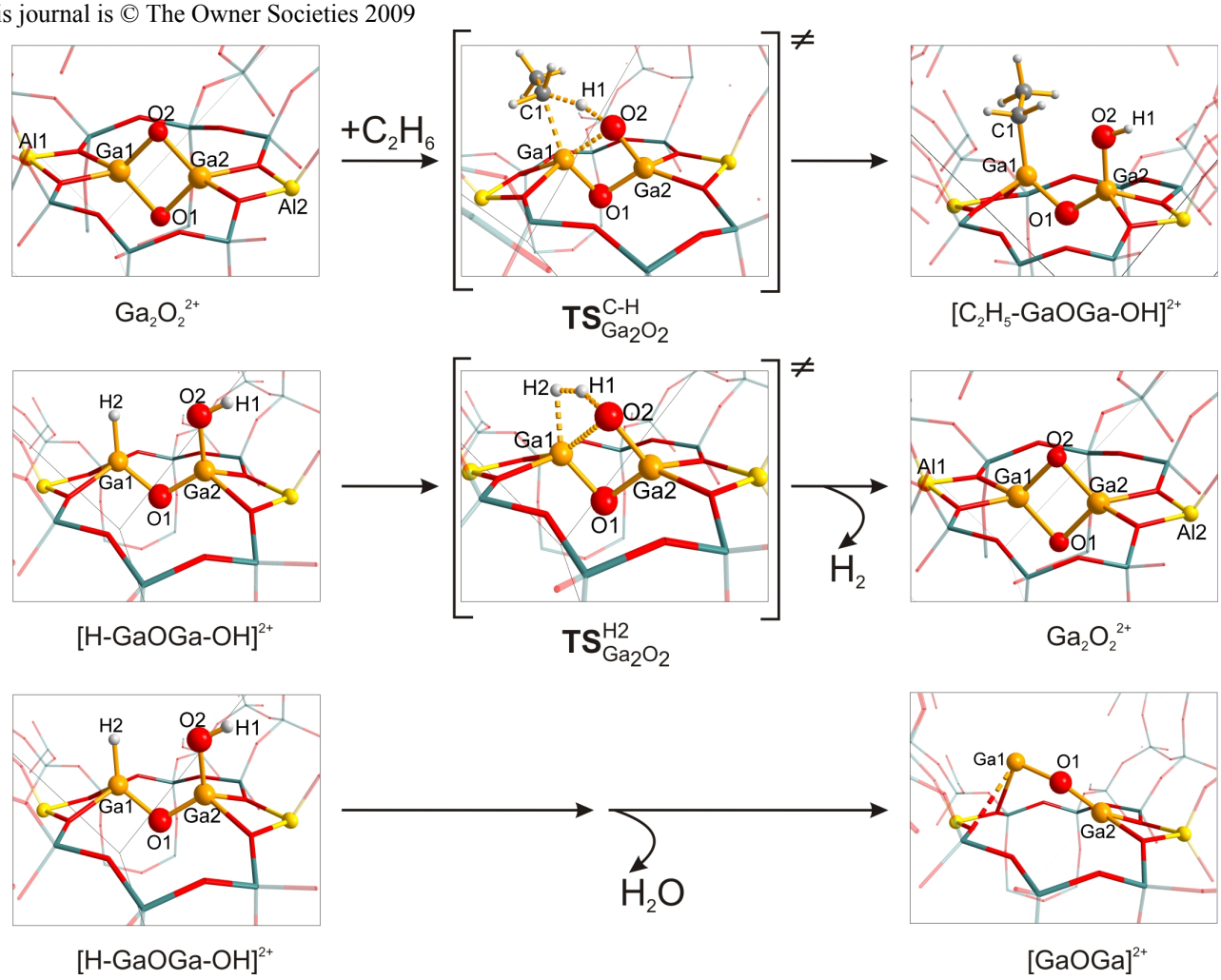

Figure S2. Optimized structures of intermediates and transition states involved in C-H activation, H_2 and H_2O desorption steps over binuclear $Ga_2O_2^{2+}$ site in mordenite model **I**.

Table S1. Selected optimized interatomic distances (Å) for intermediates and transition state structures of the important reaction steps of catalytic ethane dehydrogenation over binuclear $Ga_2O_2^{2+}$ site in mordenite model **I**.

	$Ga_2O_2^{2+}$	$TS^{C-H}_{Ga_2O_2}$	$[C_2H_5\text{-}GaOGa\text{-}OH]^{2+}$	$[H\text{-}GaOGa\text{-}OH]^{2+}$	$TS^{H2}_{Ga_2O_2}$	$[GaOGa]^{2+}$
Ga1···O1	1.859	1.877	1.828	1.818	1.991	1.947
Ga1···O2	1.861	2.018	–	–	1.860	–
Ga2···O1	1.869	1.832	1.796	1.803	1.842	1.728
Ga2···O2	1.856	1.853	1.821	1.819	1.860	–
Ga1···Ga2	2.501	2.624	3.006	2.939	2.603	3.626
C1···H1	1.098[a]	1.375	–	–	–	–
C1···Ga1	–	2.267	1.983	–	–	–
H1···O2	–	1.318	0.974	0.974	1.338	–
H2···Ga1	–	–	–	1.545	1.902	–
H1···H2	0.749[b]	–	–	–	0.970	–
Ga1-O1z	1.970	2.012	2.068	2.033	1.989	2.916
Ga1-O2z	1.970	2.039	2.036	2.016	2.016	2.488
Ga2-O3z	1.962	1.967	1.969	1.975	1.954	1.928
Ga2-O4z	1.956	1.971	2.004	1.995	1.965	1.936

[a] calculated for gas-phase ethane; [b] calculated for gas-phase dihydrogen

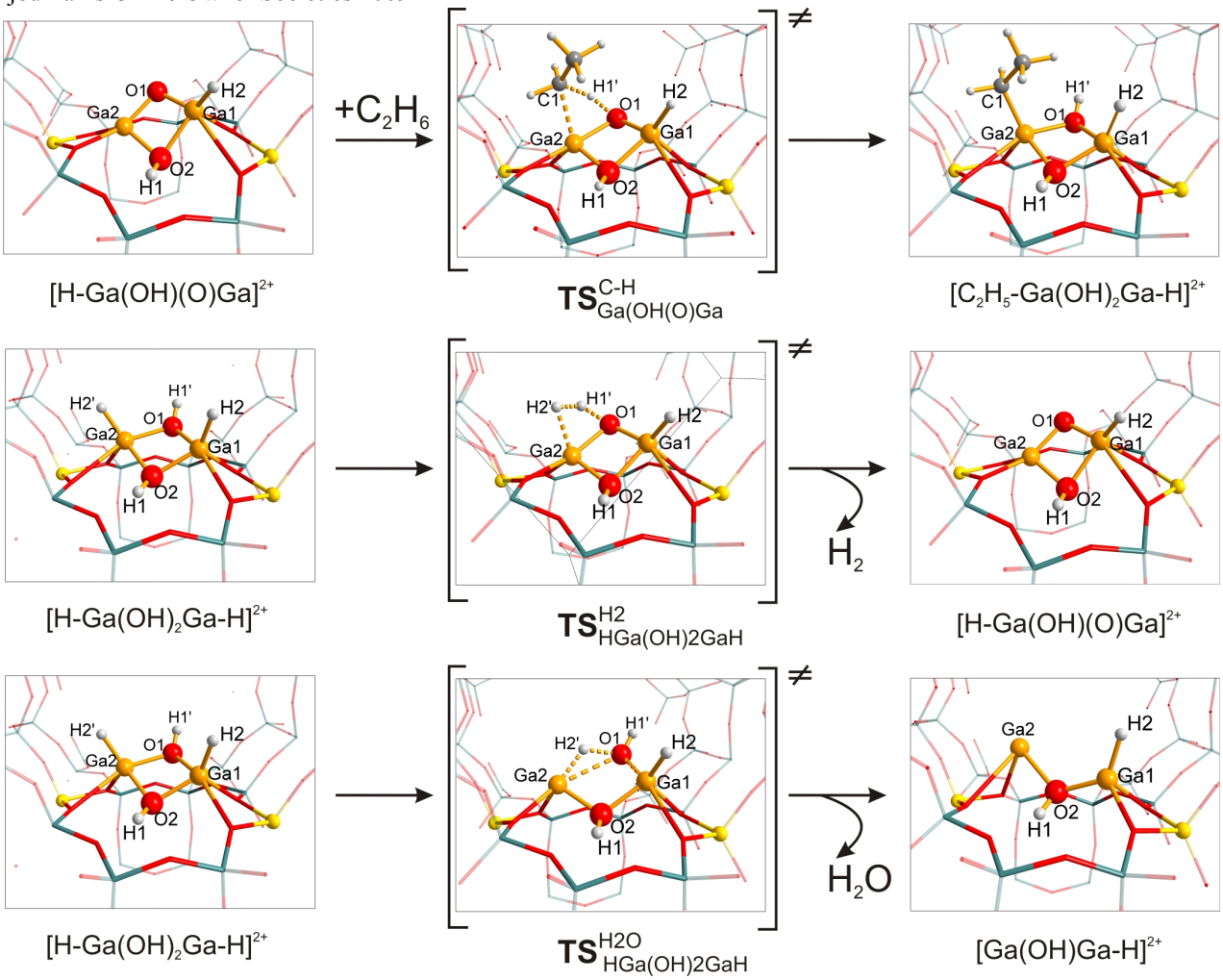

Figure S3. Optimized structures of intermediates and transition states involved in C-H activation, H_2 and H_2O desorption steps over partially hydrogenated $Ga(OH)(O)GaH^{2+}$ site in mordenite model **I**.

Table S2. Selected optimized interatomic distances (Å) for intermediates and transition state structures involved in the important reaction steps of the ethane dehydrogenation over partially hydrogenated $Ga(OH)(O)GaH^{2+}$ site.

	$[Ga(OH)(O)GaH]^{2+}$	$TS^{C\text{-}H}_{Ga(OH(O)Ga}$	$[C_2H_5Ga(OH)_2GaH]^{2+}$	$[HGa(OH)_2GaH]^{2+}$	$TS^{H2}_{HGa(OH)2GaH}$	$TS^{H2O}_{HGa(OH)2GaH}$	$[Ga(OH)GaH]^{2+}$
Ga1···O1	1.870	1.880	1.995	2.014	1.890	1.927	–
Ga1···O2	2.047	1.980	1.922	1.922	1.993	1.930	1.851
Ga2···O1	1.813	1.940	1.972	1.951	1.909	2.754	–
Ga2···O2	1.903	1.907	1.949	1.933	1.907	1.972	2.205
Ga1···Ga2	2.745	2.832	2.946	2.974	2.836	3.191	3.562
Ga1···H2	1.548	1.547	1.548	1.548	1.546	1.547	1.540
O2···H1	0.988	0.982	0.989	0.991	0.983	0.979	0.980
C1···H1’	1.098	1.342	–	–	–	–	–
C1··Ga2	–	2.256	1.979	–	–	–	–
H1’···O1	–	1.362	0.972	0.971	1.399	0.977	–
H2’···Ga2	–	–	–	1.548	1.891	1.647	–
H2’···H1’	–	–	–	–	0.956	–	–
H2’···O1	–	–	–	–	–	1.514	–
Ga1-O1z	2.867	2. 842	2.321	2.291	2.833	2.536	2.015
Ga1-O2z	2.043	2. 004	1.987	1.992	2.000	2.012	2.012
Ga2-O3z	1.947	2.120	2.565	2.495	2.052	2.121	2.760
Ga2-O4z	1.971	1.964	2.003	1.987	1.940	2.043	2.432

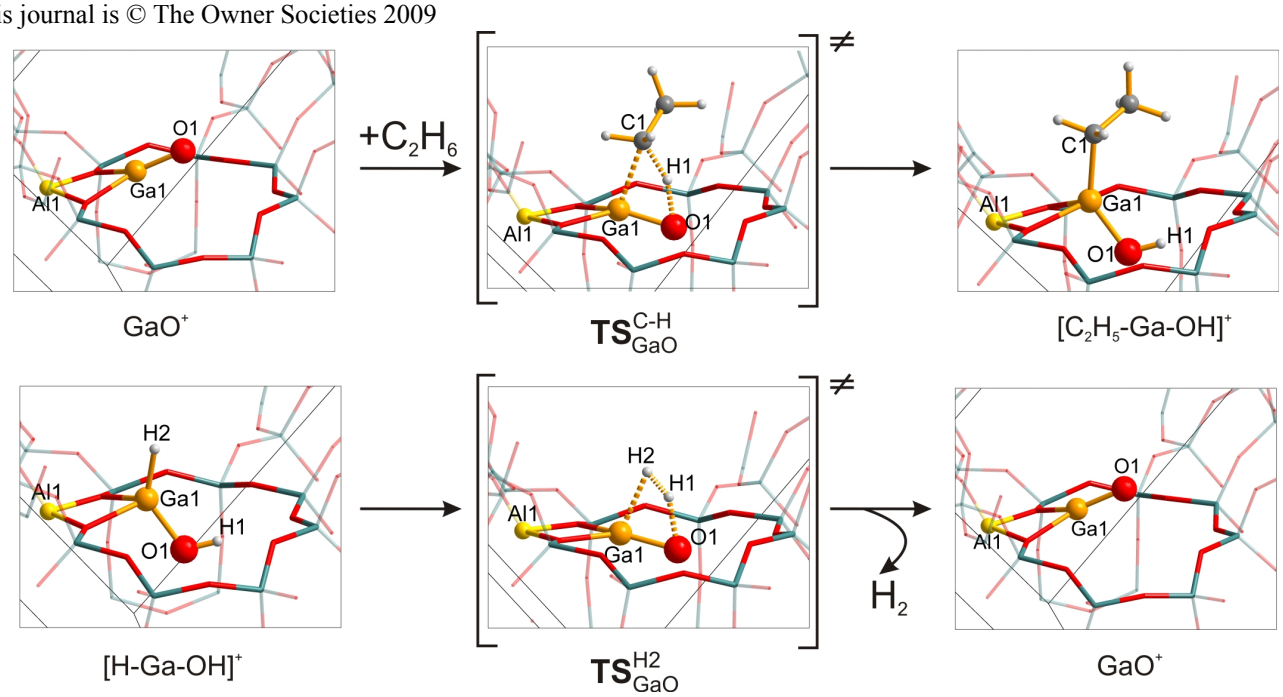

Figure S4. Optimized structures of intermediates and transition states involved in C-H activation and H_2 desorption steps over isolated GaO^+ site in high-silica mordenite

Table S3. Selected optimized interatomic distances (Å) for intermediates and transition state structures involved in C-H activation and H_2 recombination steps of ethane dehydrogenation over isolated GaO^+ site in mordenite.

	GaO^+	$TS^{C\text{-}H}_{GaO}$	$[C_2H_5\text{-}Ga\text{-}OH]^+$	$[H\text{-}Ga\text{-}OH]^+$	TS^{H2}_{GaO}
Ga1···O1	1.693	1.754	1.821	1.812	1.744
C1···H1	1.098[a]	1.388	–	–	–
C1···Ga1	–	2.281	1.979	–	–
H1···O2	–	1.435	0.977	0.978	1.521
H2···Ga1	–	–	–	1.549	1.969
H1···H2	0.749[b]	–	–	–	0.939

[a] calculated for gas-phase ethane; [b] calculated for gas-phase dihydrogen