Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Hydrogenous spinel γ-alumina structure

Jinshi Dong,[a] Jun Wang,[a] Lu Shi,[d] Jiaqiang Yang,[d] Jianqiang Wang,[a] Bin Shan,[d] and Meiqing Shen*[a, b, c]

[a] Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, P.R. China

[b] State Key Laboratory of Engines, Tianjin University, Tianjin 300072, P.R. China

[c] Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P.R. China

[d] State Key Laboratory of Materials Processing and Die and Mould Technology and School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, P.R. China

*Corresponding Authors: Tel./ Fax.: (+86) 22-27407002.

Email address: mqshen@tju.edu.cn (Prof. Shen)

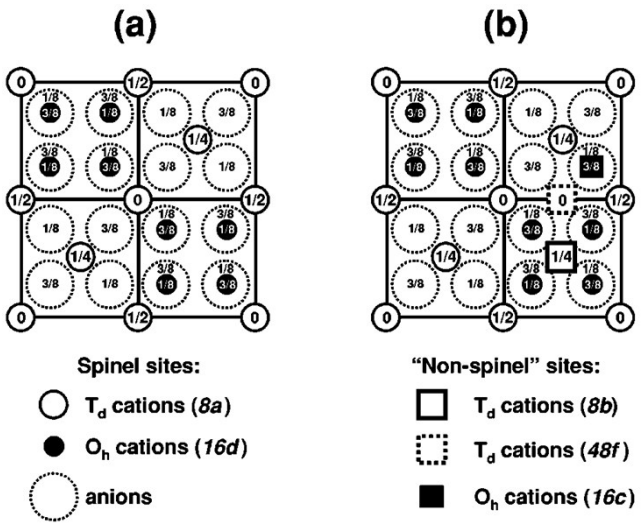


Fig. S1 Atomic sites in the spinel structure along the (001) projection. (a) normal spinel cation sites: T_d (8a) and O_h (16d). (b) nonspinel cation sites: T_d (8b and 48f) and O_h (16c).

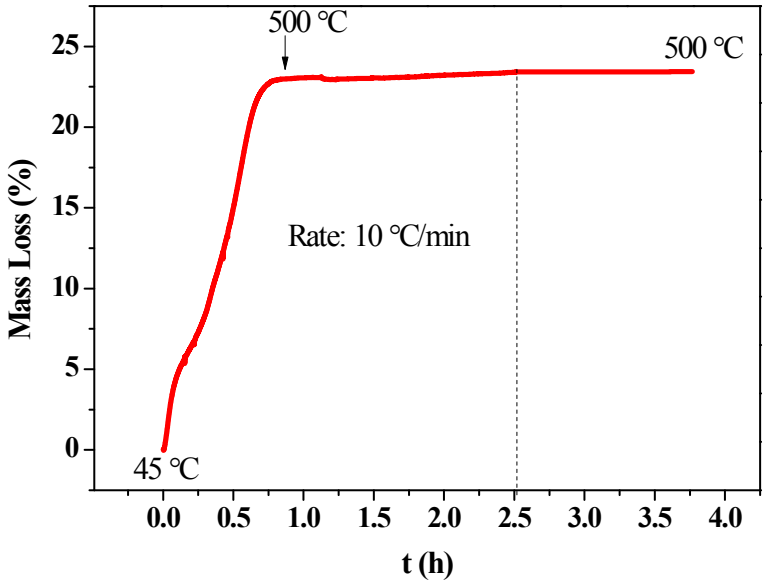


Fig. S2 Weight-loss profile during the forming of LT γ-Al_2O_3 structure from pseudo-boehmite (PSB). The heating rate is 10 ºC/min and the sample was kept at 500 ºC for 3 h. After treatment for 2.5 h (including the heat up process), no more mass loss was observed meaning that the dehydration was completed at 500 ºC in less than 3 h.

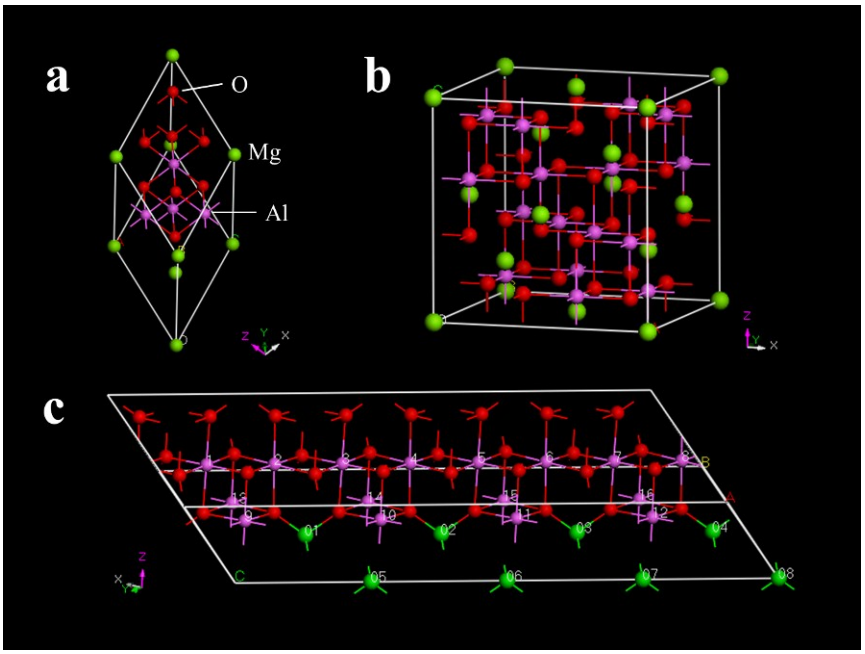
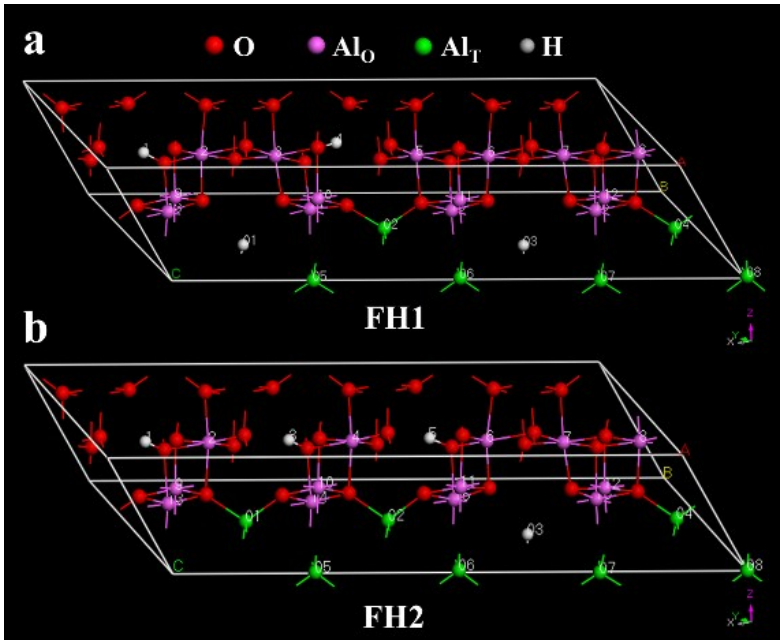
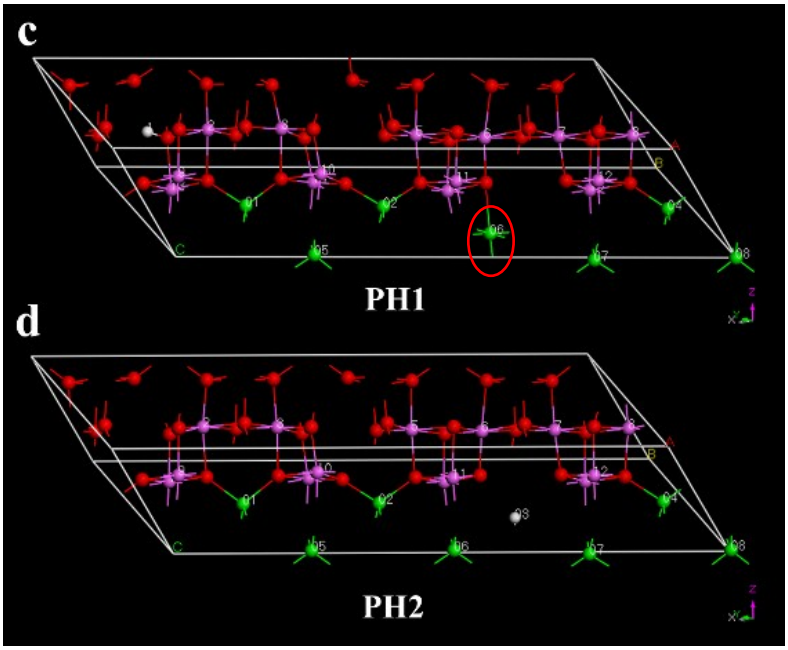


Fig. S3 The structure models of MgAl spinel. a, primitive cell (Mg2Al4O8); b, conventional cell (Mg8Al16O32); c, 4* primitive cell along [110] (Mg8Al16O32). Green, purple and red balls represent Mg, Al and O, respectively.


a
O
Al$_O$
Al$_T$
H
FH1
b
FH2


c
PH1
d
PH2

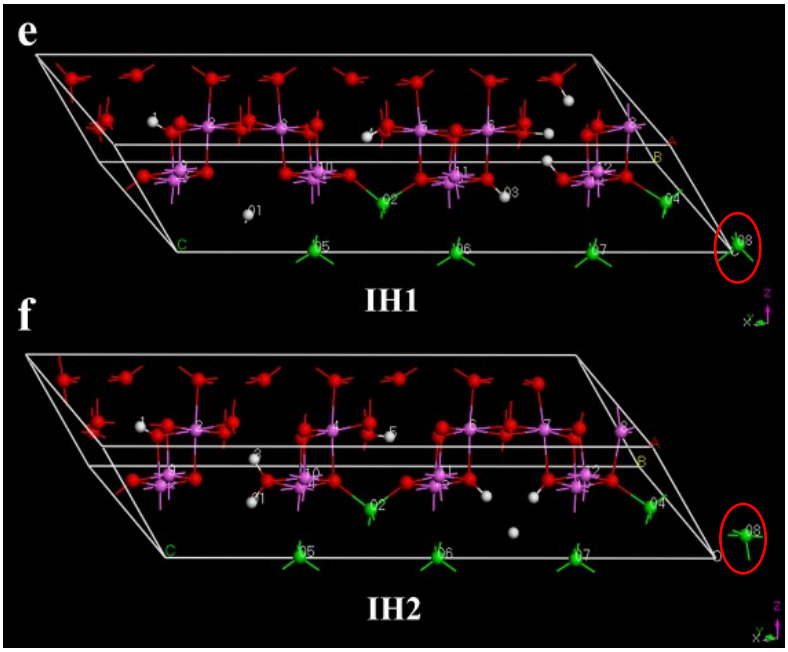


Fig. S4 The relaxed H spinel γ-Al_2O_3 LT structures with the minimum energies of every given cell composition. Green, purple, red and white balls represent Al_T, Al_O, O and H, respectively. the H-O distances are ~1.0 Å in all cases. The Al atoms in red circles are nonspinel Al sites.

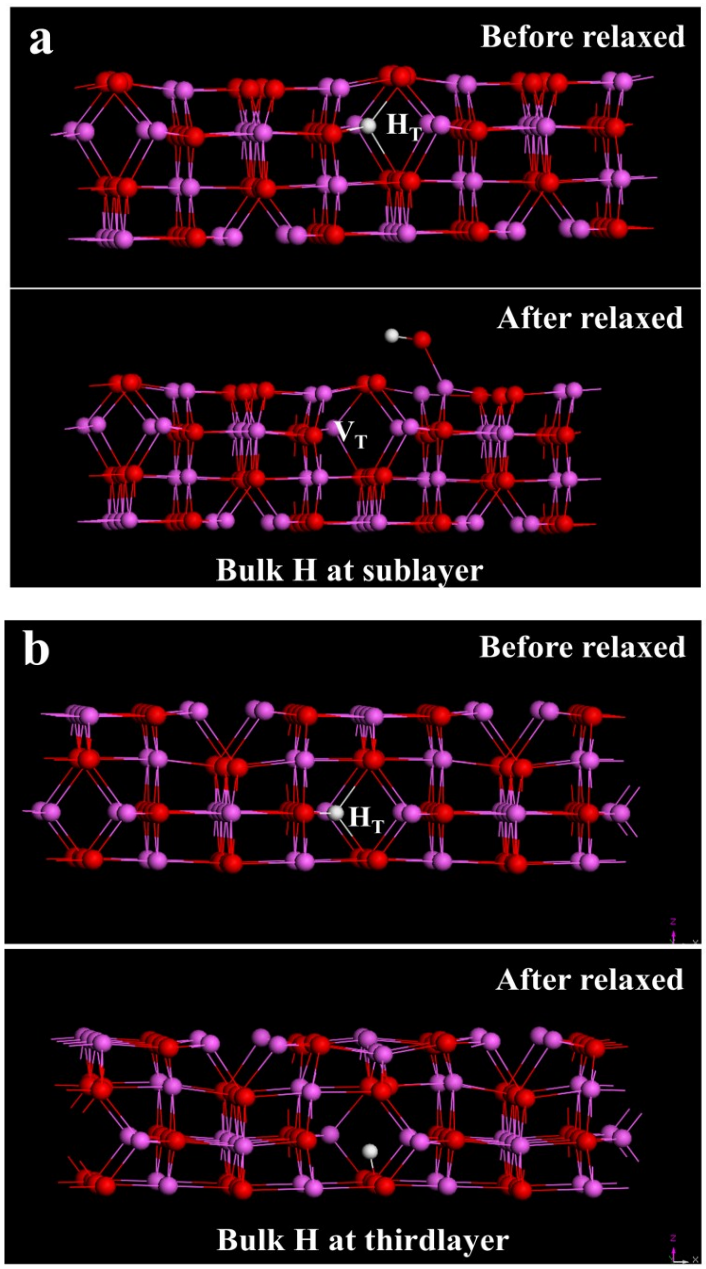


Fig. S5 Surface (110) structure with bulk H at (a) sublayer and (b) thirdlayer. Purple, red and white balls represent Al, O and H, respectively.

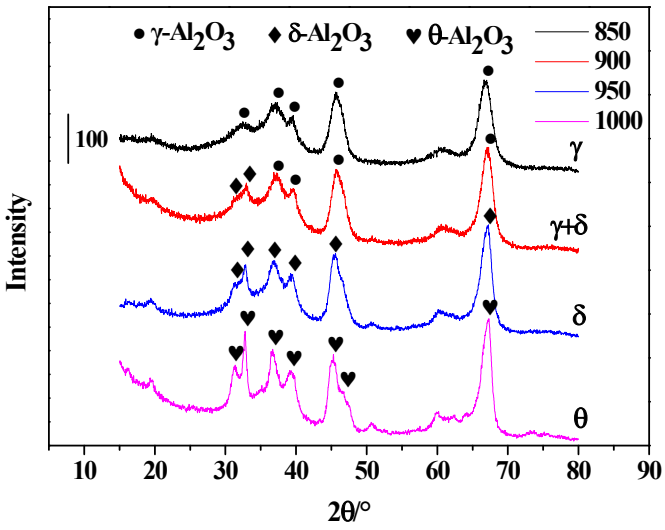


Fig. S6 XRD patterns of the alumina sample calcinated at 850- 1000 ºC.

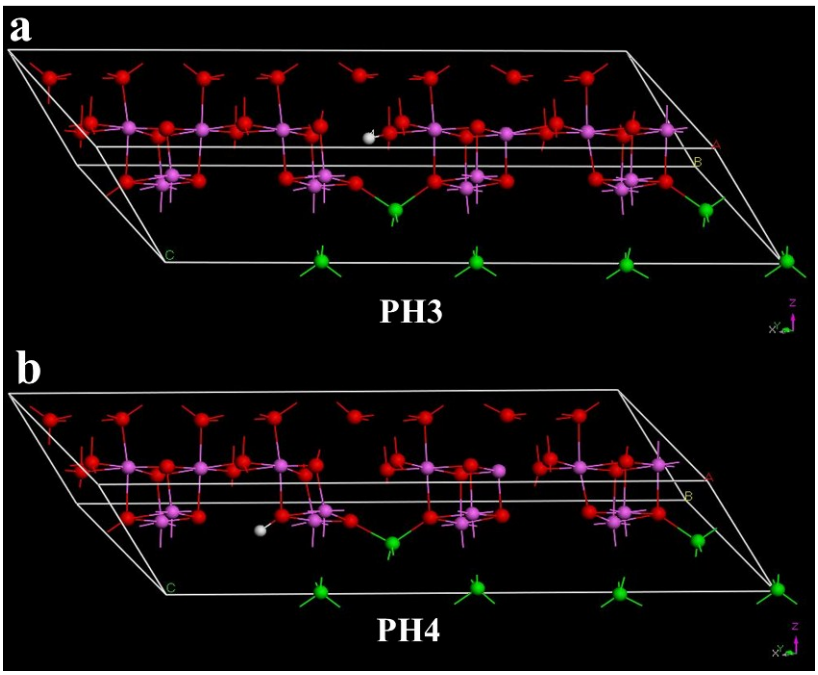


Fig. S7 The relaxed H spinel γ-Al_2O_3 HT structures with the minimum energies of every given cell composition. Green, purple, red and white balls represent Al_T, Al_O, O and H, respectively.

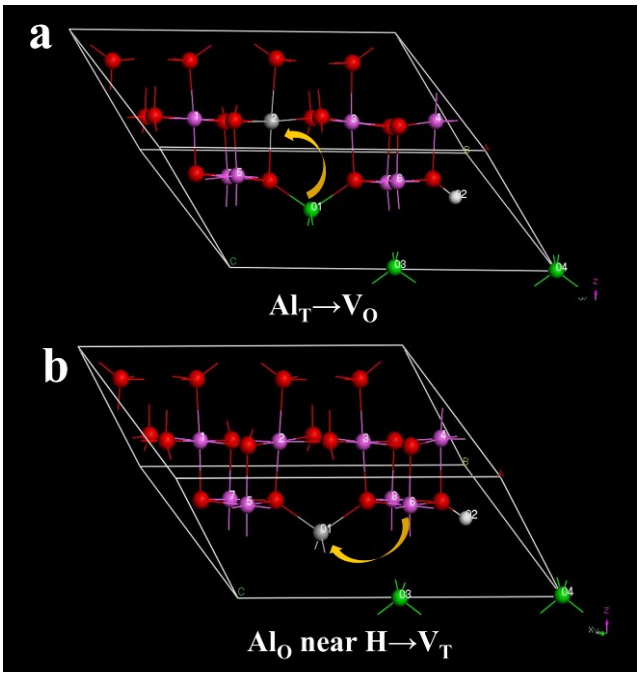


Fig. S8 The migration paths for Al in LT γ-Al_2O_3. a, $Al_T \rightarrow V_O$; b, AlO near $H_T \rightarrow V_T$. Only half of the unit cell (2* primitive cell) shown. The gray ball represents the relaxed final state of the migrating atom. Green, purple, red and white balls represent Al_T, Al_O, O and H, respectively.

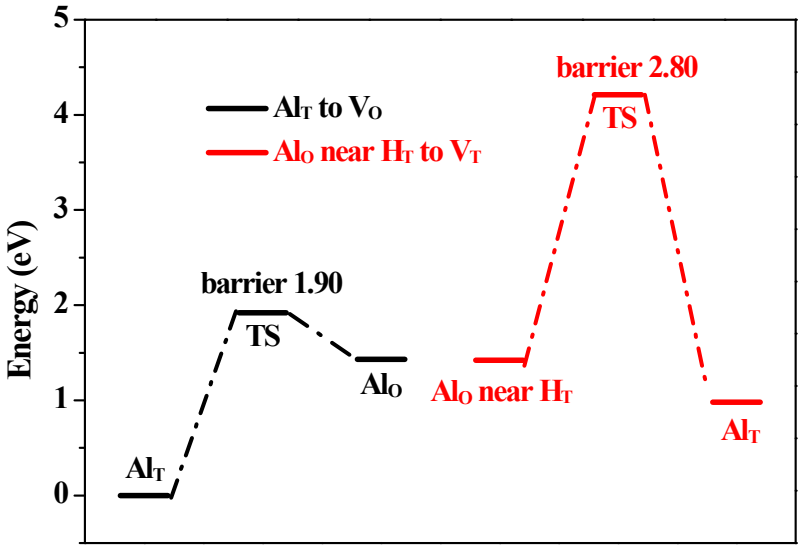


Fig. S9 Energy barriers for the migration paths shown in Fig. S8. TS stands for transition state, and the energy barriers are shown in the figure.

Table S1 Thermodynamic parameters of H_2O.

Parameter	Value
ω_i	291.6, 271.6, 206.1, 132.4, 128.8, 119.1 meV
E_{ZPE}	0.575 eV
$\Sigma C_p\,dT\ (T=773\ K)$	0.239 eV
$\Sigma C_p\,dT\ (T=1073\ K)$	0.365 eV
$S_g\,(T=773\ K)$	0.0023 eV/K
$S_g\,(T=1073\ K)$	0.0024 eV/K