

Supplementary Information

Trends in the Adsorption and Reactivity of Hydrogen on Magnesium Silicate Nanoclusters

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1. The extent of BSSE in our calculations for a range of H atom physisorption and chemisorption sites is detailed in tables (i) and (ii) below. See main text for discussion. $E_{\text{bind}}^{\text{c}}$ denotes the BSSE-corrected E_{bind} value in each case.

Table (i) : Physisorption

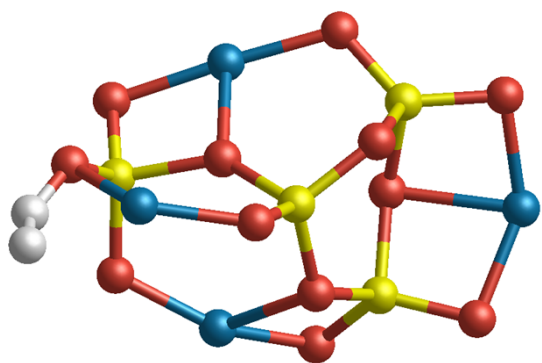
	Adsorption Site	E_{bind} (kJ/mol)	BSSE (%)	$E_{\text{bind}}^{\text{c}}$ (kJ/mol)
Nanopyroxene	P2	11	38	7
Nano-olivine_a	P1	7	45	4
	P2	9	41	5
	P3	17	18	14

Table (ii) : Chemisorption

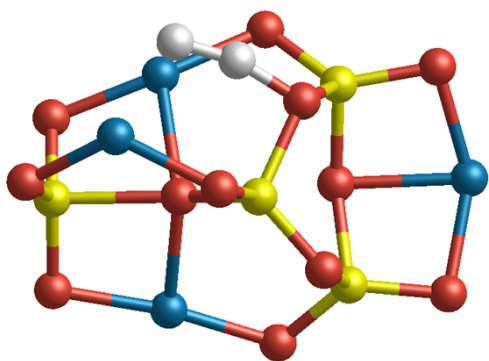
	Adsorption Site	E_{bind} (kJ/mol)	BSSE (%)	$E_{\text{bind}}^{\text{c}}$ (kJ/mol)
Nanopyroxene	C1	69	7	64
		91	7	85
		200	2	195
Nano-olivine_a	C1	43	9	37
		92	5	87
		146	3	141
		272	2	267
	C2	91	4	87
		105	4	101

2. Transition state structures corresponding to the “TS” labels in Fig. 10. Subscripts correspond to the figure showing the corresponding initial $\text{H}_{\text{chem}}^+ + \text{H}_{\text{chem}}^-$ configuration.

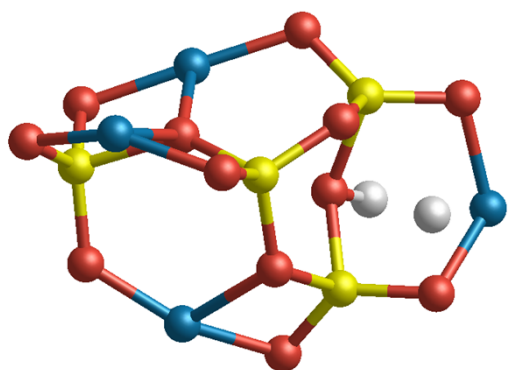
TS_{6b}



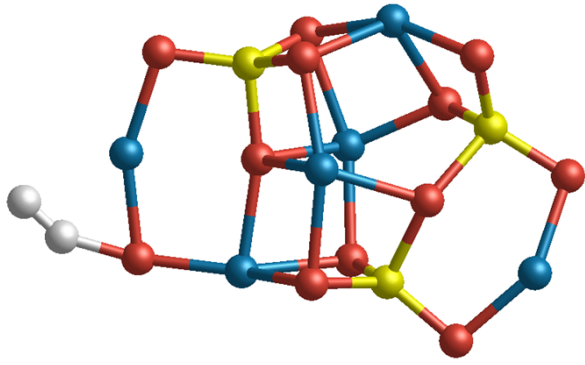
TS_{6d}



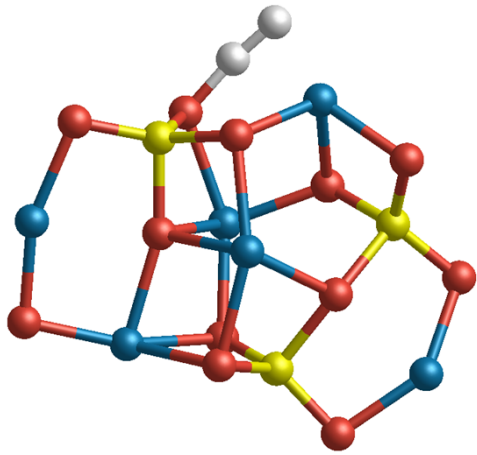
TS_{6e}



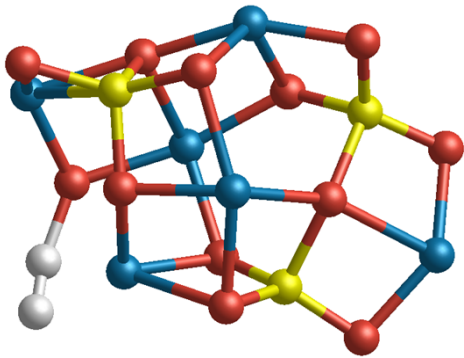
TS_{7d}



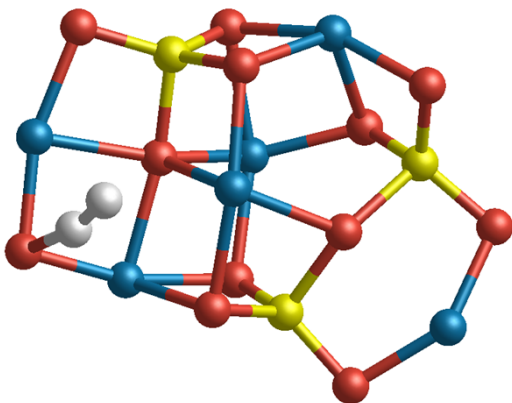
TS_{7g}



TS_{9a}



TS_{9b}



3. Lists of calculated vibrational frequencies for all transition states considered. The figure corresponding to the initial $H^+_{chem.}+H^-_{chem}$ configuration is provided in parentheses. The single imaginary frequency is labelled with an "i" in each case.

Species	Frequency (cm-1)
TS _{6a}	1744 1688 1321 1155 1127 1118 1095 1066 1021 1000 971 956 928 893 889 836 774 741 723 717 704 645 634 619 602 567 536 526 494 485 472 451 437 420 403 392 371 354 335 327 295 284 275 264 258 246 235 223 208 200 176 155 153 153 140 130 121 86 55 1337i
TS _{6b}	1776 1733 1305 1143 1130 1117 1095 1014 1005 997 970 949 930 917 870 822 765 741 730 714 699 663 652 622 603 593 560 557 519 501 472 459 450 420 411 395 380 358 342 328 313 287 271 265 250 246 230 225 207 195 186 163 152 148 137 101 97 87 56 1367i
TS _{6d}	1603 1511 1430 1175 1153 1143 1114 11089 1028 978 952 924 911 884 846 804 749 743 730 718 702 691 651 624 609 595 584 546 529 500 485 455 443 428 407 394 384 367 363 322 314 300 288 280 263 247 244 223 4 205 189 176 164 152 139 126 109 76 66 1170i
TS _{6e}	1817 1461 1400 1192 1167 1128 1107 1102 1071 1034 997 967 942 930 842 782 743 730 719 714 661 640 632 616 593 590 589 551 534 506 482 466 444 430 410 400 392 372 350 328 323 296 286 273 262 256 244 226 219 207 190 168 155 148 145 131 124 96 45 769i
TS _{6f}	1795 1631 1263 1154 1135 1088 1067 1051 1031 1023 974 972 931 896 882 876 758 744 732 713 705 659 639 617 602 581 550 529 520 485 470 455 439 416 409 398 373 354 336 323 305 280 271 267 245 242 232 218 209 193 172 158 154 148 158 154 148 140 98 87 71 58 1373i
TS _{7b}	1626 1484 1317 1171 1138 1117 1041 983 948 872 912 938 855 809 760 756 696 691 648 646 616 612 595 583 564 552 516 511 506 437 473 470 454 434 421 421 405 385 375 348 340 329 323 312 303 290 275 272 263 241 240 221 205 202 194 172 166 149 130 121 112 80 1111i
TS _{7c}	1779 1679 1328 1121 1115 1099 1036 990 946 929 880 877 865 840 791 764 693 675 653 629 611 604 590 582 557 552 535 519 502 490 482 454 443 424 418 400 392 376 348 339 329 321 313 305 286 278 268 266 252 248 235 219 203 199 176 165 155 148 140 128 92 82 1371i
TS _{7d}	2138 1681 1227 1133 1120 1093 1016 946 932 908 884 872 844 779 758 741 709 668 636 631 623 603 602 581 561 554 545 531 505 490 478 456 442 422 416 397 393 374 356 346 327 321 315 302 281 276 272 251 247 238 231 206 194 179 169 158 148 136 133 96 87 61 999i

TS _{7e}	1944 1484 1165 1147 1121 1107 1002 969 925 902 877 855 847 809 774 748 680 674 658 627 599 585 566 553 544 539 523 512 494 463 457 435 419 405 388 386 382 362 357 339 334 312 301 296 279 259 256 252 231 221 218 192 181 164 159 147 139 121 74 63 44 27 420i
TS _{7f}	1795 1631 1263 1154 1135 1088 1067 1051 1031 1023 974 972 931 896 882 876 758 744 732 713 705 659 639 617 602 581 550 529 520 485 470 455 439 416 409 398 373 354 336 323 305 280 271 267 245 242 232 218 209 193 172 158 154 148 158 154 148 140 98 87 71 58 1373i
TS _{7g}	2185 1620 1383 1127 1097 1094 1063 1006 949 939 905 889 877 838 789 773 736 689 673 634 622 605 587 582 567 548 523 509 497 487 472 457 442 430 424 419 400 384 379 338 336 332 322 306 288 273 267 263 255 240 223 208 198 176 168 162 154 139 135 124 97 86 1037i
TS _{9a}	2280 1423 1320 1130 1116 1094 1010 948 945 908 875 861 828 781 746 741 671 656 645 625 615 610 606 592 569 554 538 532 506 500 491 481 469 437 432 420 400 377 360 353 339 326 322 317 295 287 282 270 250 244 230 226 182 165 155 148 133 120 88 81 696i
TS _{9b}	2196 1682 1263 1130 1104 1100 1017 994 970 912 890 871 850 775 748 738 675 670 646 630 625 612 586 575 558 541 527 519 510 481 471 465 446 441 431 419 393 387 365 346 340 334 311 302 288 276 270 260 253 249 226 222 212 205 194 178 166 157 139 135 104 92 809i

4. Plot of $2H_{\text{chem}} \rightarrow H_2$ recombination barrier height versus the binding energy of one H atom chemisorbed to the respective bare cluster in a C1 mode (i.e. H^+_{chem}) for all reaction paths on nano-olivine_a and nano-pyroxene clusters. The labelling of the data points follows that in Figs. 6, 7 and 9. Data from Goumans et al. (article ref [22]) corresponding to the foresterite (010) surface and from Kerkeni and Bromley (article ref [21]) corresponding to the nano-olivine_c cluster are also shown.

