Table S2. Optimized Geometrical Parameters of the Bridging Hydroxyl Group Al-O-Si for PYH^+/ZO^- Adsorption Complexes with One to Four Al Atoms Calculated at the PBE and PBE-D3 (in brackets) Levels in Cluster and Periodic Models.

PYH^+/ZO^- Adsorption Complexes	Cluster Model (32T)			Periodic Model (96T)		
	Al-O[a]	Si-O[a]	AlOSi[b]	Al-O[a]	Si-O[a]	AlOSi[b]
1 Al						
$Al1_{ads}$	1.836(1.833)	1.653(1.651)	124.5(123.9)	1.772(1.774)	1.608(1.609)	130.5(129.4)
$Al2_{ads}$	1.804(1.801)	1.631(1.629)	130.2(129.2)	1.760(1.756)	1.602(1.601)	138.1(137.8)
$Al3_{ads}$	1.821(1.817)	1.635(1.633)	137.3(137.5)	1.776(1.778)	1.603(1.603)	141.6(141.9)
$Al4_{ads}$	1.864(1.863)	1.632(1.632)	126.9(125.5)	1.772(1.772)	1.604(1.605)	131.7(130.4)
2 Al						
$Al1_{ads}Al2$	1.836(1.833)	1.656(1.655)	124.5(124.2)	1.772(1.772)	1.609(1.609)	131.0(129.8)
$Al1_{ads}Al3$	1.844(1.843)	1.660(1.659)	125.4(124.9)	1.774(1.773)	1.611(1.611)	130.5(129.8)
$Al1_{ads}Al4$	1.837(1.834)	1.654(1.652)	124.7(124.2)	1.773(1.773)	1.608(1.608)	130.9(129.6)
$Al2_{ads}Al1$	1.803(1.800)	1.633(1.631)	132.9(132.0)	1.763(1.760)	1.606(1.604)	137.0(136.5)
$Al2_{ads}Al3$	1.799(1.802)	1.633(1.632)	130.5(129.5)	1.756(1.754)	1.608(1.607)	137.6(137.2)
$Al2_{ads}Al4$	1.799(1.796)	1.632(1.630)	131.1(130.1)	1.758(1.754)	1.605(1.604)	138.1(136.8)
$Al3_{ads}Al1$	1.825(1.820)	1.637(1.636)	138.2(138.6)	1.776(1.777)	1.606(1.605)	141.4(141.7)
$Al3_{ads}Al2$	1.810(1.807)	1.634(1.633)	136.3(136.3)	1.771(1.769)	1.610(1.09)	138.5(139.6)
$Al3_{ads}Al4$	1.821(1.817)	1.636(1.634)	136.2(136.1)	1.774(1.774)	1.603(1.602)	139.5(142.0)
$Al4_{ads}Al1$	1.863(1.861)	1.632(1.632)	127.1(125.7)	1.773(1.771)	1.606(1.606)	131.4(130.2)
$Al4_{ads}Al2$	1.859(1.860)	1.635(1.635)	129.3(126.8)	1.771(1.773)	1.609(1.609)	131.5(130.2)
$Al4_{ads}Al3$	1.865(1.865)	1.633(1.633)	125.3(125.3)	1.775(1.773)	1.607(1.606)	131.3(130.4)
3 Al						
$Al1_{ads}Al2Al3$	1.841(1.838)	1.663(1.662)	125.6(125.2)	1.777(1.777)	1.623(1.613)	130.7(130.0)
$Al1_{ads}Al2Al4$	1.837(1.834)	1.657(1.656)	124.7(124.4)	1.775(1.772)	1.610(1.609)	130.9(130.3)
$Al1_{ads}Al3Al4$	1.840(1.839)	1.661(1.660)	126.1(125.3)	1.776(1.773)	1.611(1.611)	130.9(129.5)
$Al2_{ads}Al1Al3$	1.802(1.800)	1.634(1.632)	131.9(130.8)	1.757(1.752)	1.610(1.608)	136.5(135.9)
$Al2_{ads}Al1Al4$	1.805(1.803)	1.635(1.633)	132.4(131.2)	1.758(1.757)	1.607(1.606)	135.9(136.5)
$Al2_{ads}Al3Al4$	1.794(1.794)	1.633(1.632)	131.4(130.0)	1.754(1.749)	1.610(1.609)	137.4(136.9)
$Al3_{ads}Al1Al2$	1.814(1.810)	1.635(1.634)	134.9(135.0)	1.770(1.768)	1.612(1.612)	139.7(139.1)
$Al3_{ads}Al1Al4$	1.826(1.821)	1.638(1.637)	137.2(137.4)	1.774(1.776)	1.606(1.606)	138.8(141.7)
$Al3_{ads}Al2Al4$	1.811(1.807)	1.635(1.634)	135.3(135.3)	1.767(1.769)	1.609(1.608)	139.3(141.8)
$Al4_{ads}Al1Al2$	1.858(1.859)	1.635(1.636)	129.4(126.9)	1.772(1.771)	1.609(1.609)	131.6(130.4)
$Al4_{ads}Al1Al3$	1.864(1.863)	1.633(1.633)	127.3(125.6)	1.776(1.773)	1.607(1.606)	131.3(130.4)
$Al4_{ads}Al2Al3$	1.859(1.861)	1.636(1.637)	129.8(126.8)	1.776(1.774)	1.610(1.610)	131.5(130.3)
4 Al						
$Al1_{ads}Al2Al3Al4$	1.843(1.839)	1.664(1.663)	125.9(125.4)	1.776(1.773)	1.612(1.612)	131.3(130.2)
$Al2_{ads}Al1Al3Al4$	1.797(1.794)	1.635(1.633)	134.4(133.4)	1.754(1.751)	1.610(1.611)	136.3(136.9)
$Al3_{ads}Al1Al2Al4$	1.815(1.812)	1.634(1.635)	134.1(133.7)	1.770(1.768)	1.612(1.610)	138.6(141.8)
$Al4_{ads}Al1Al2Al3$	1.858(1.860)	1.636(1.637)	129.9(126.7)	1.776(1.775)	1.610(1.610)	131.5(130.5)

[a]In Å; [b]In deg.