Supporting Information

Dual Effects of Water Vapor on Ceria-Supported Gold Clusters

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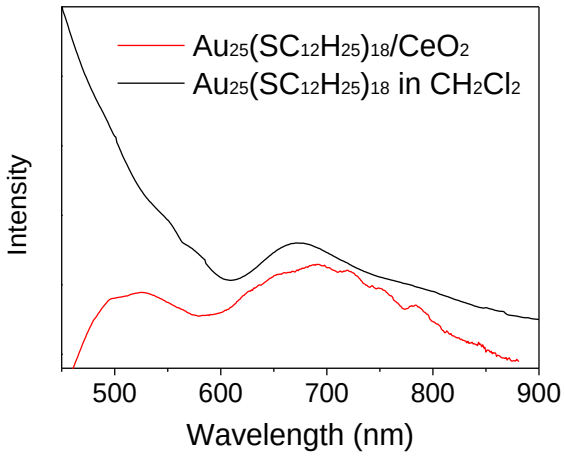

Figure S1. Diffuse reflectance optical spectrum of the fresh $Au_{25}(SC_{12}H_{25})_{18}/CeO_2$ (red) and comparison with the solution spectrum of $Au_{25}(SC_{12}H_{25})_{18}$ (black).

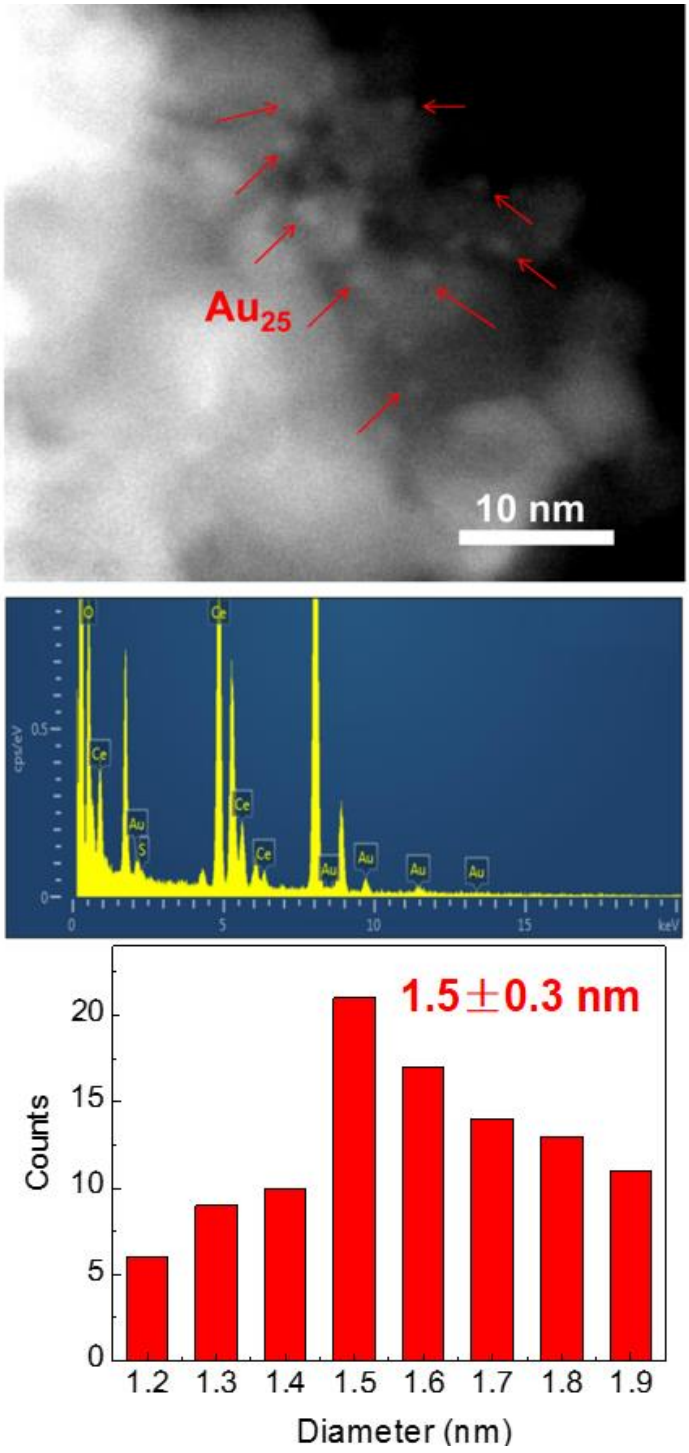

Figure S2. TEM image of the fresh $Au_{25}(SC_{12}H_{25})_{18}/CeO_2$ catalyst with EDX analysis. The size of the gold cluster is ca. 1.5±0.3 nm.

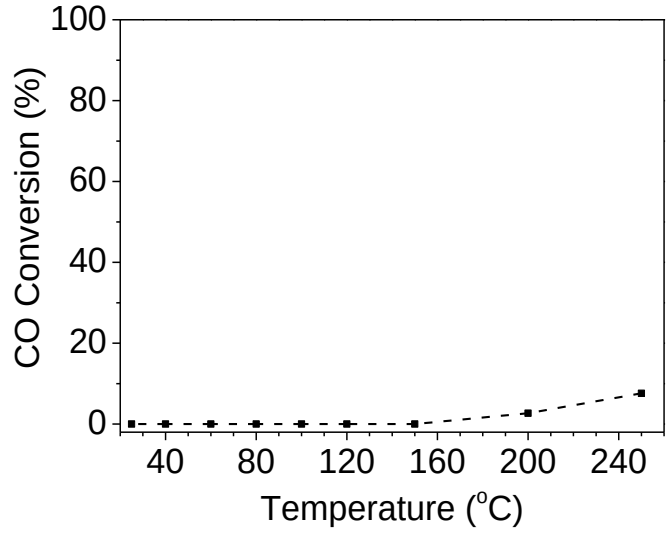

Figure S3. Blank experiment for the CO oxidation using only plain CeO_2 as the catalyst in the presence of water.

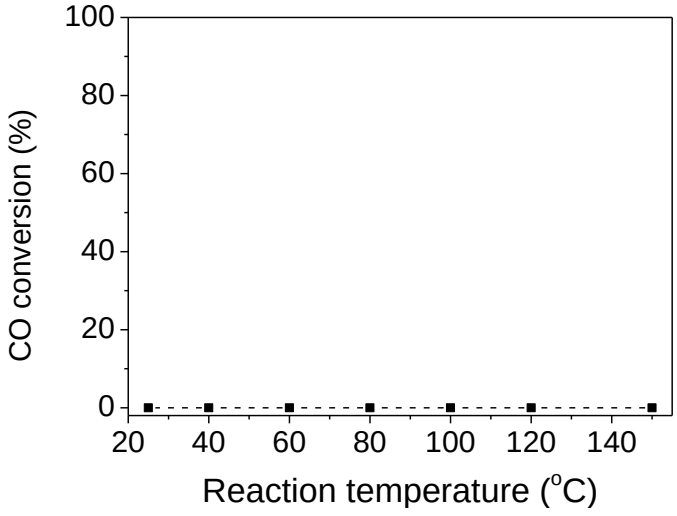

Figure S4. Control experiment for the CO oxidation using $[Au(I)\text{-}SR]_n$ polymers as the catalyst in the presence of water.

Table S1. Physical property of fresh Au_{25}/CeO_2 and Au_{25}/CeO_2 after the 373K treatment in the presence of water vapor.

Samples	V_{pore} (cm^3/g)[a]	S_{BET} (cm^2/g)[c]	Average pore diameter (nm)[c]
Au_{25}/CeO_2	32.64	15.13	28.6
Au_{25}/CeO_2-vapor (373K)	67.64	16.23	29.4

[a]V_{pore} was measured at $P/P_0 = 0.98$. [b]BET method. [c]BJH desorption average pore diameter.

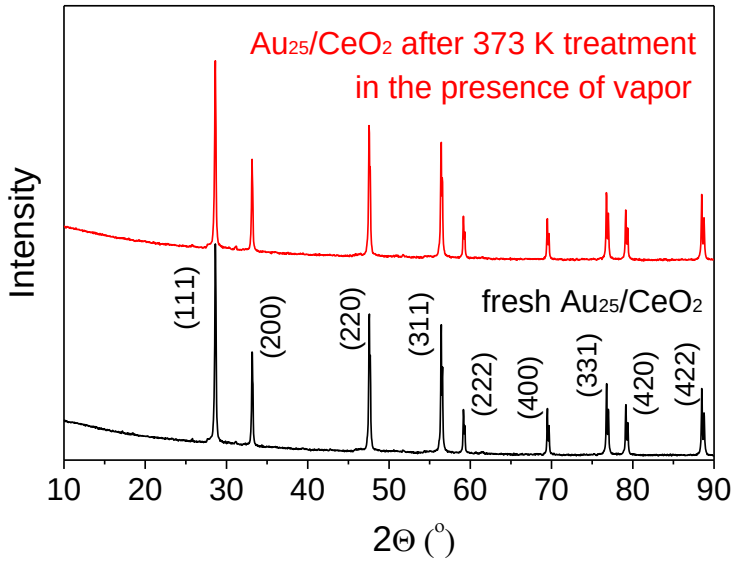

Figure S5. XRD patterns of the fresh Au_{25}/CeO_2 and Au_{25}/CeO_2 after the 373K treatment in the presence of water vapor.

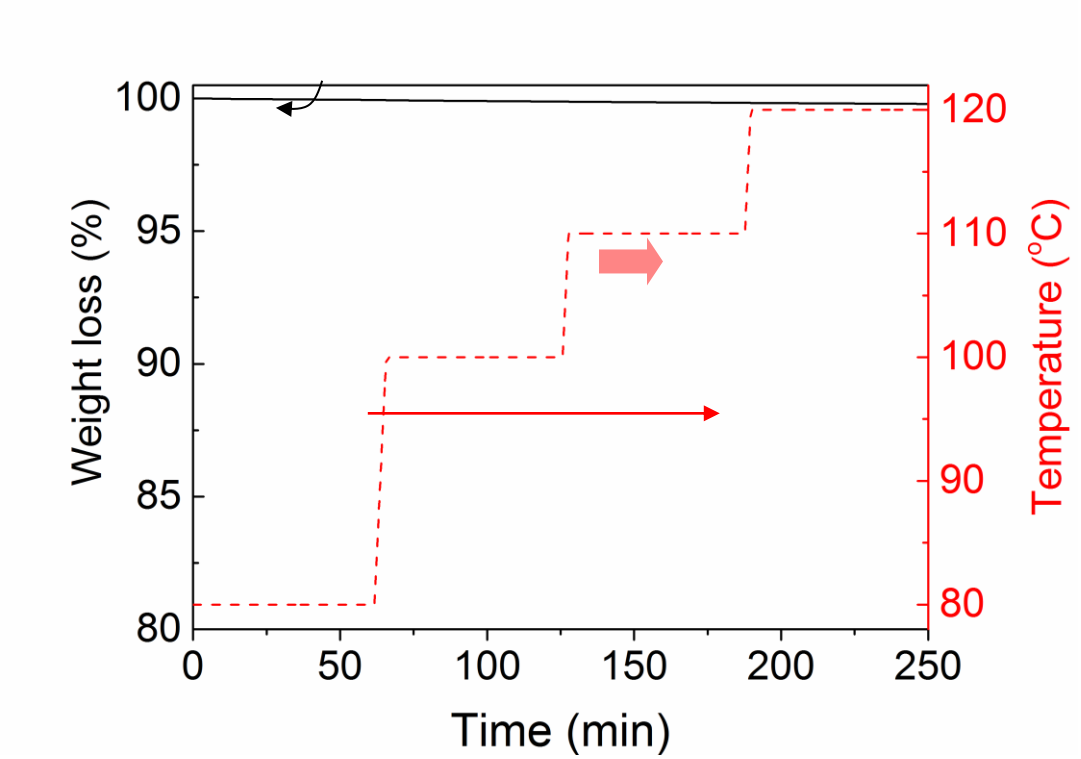

Figure S6. Temperature-programmed thermo-gravimetric analysis (TGA) of the $Au_{25}(SC_{12}H_{25})_{18}/CeO_2$ catalyst in the presence of a dry atmosphere. The sample was first treated at 60 ^{o}C in vacuum for 6 h (not shown in the figure), and then it was tested in TGA under isothermal conditions at 80/100/110/120 ^{o}C (shown as different plateaus in the red curve), respectively. There was no weight loss (see top black curve) at plateaus of 80/100/110/120 ^{o}C.

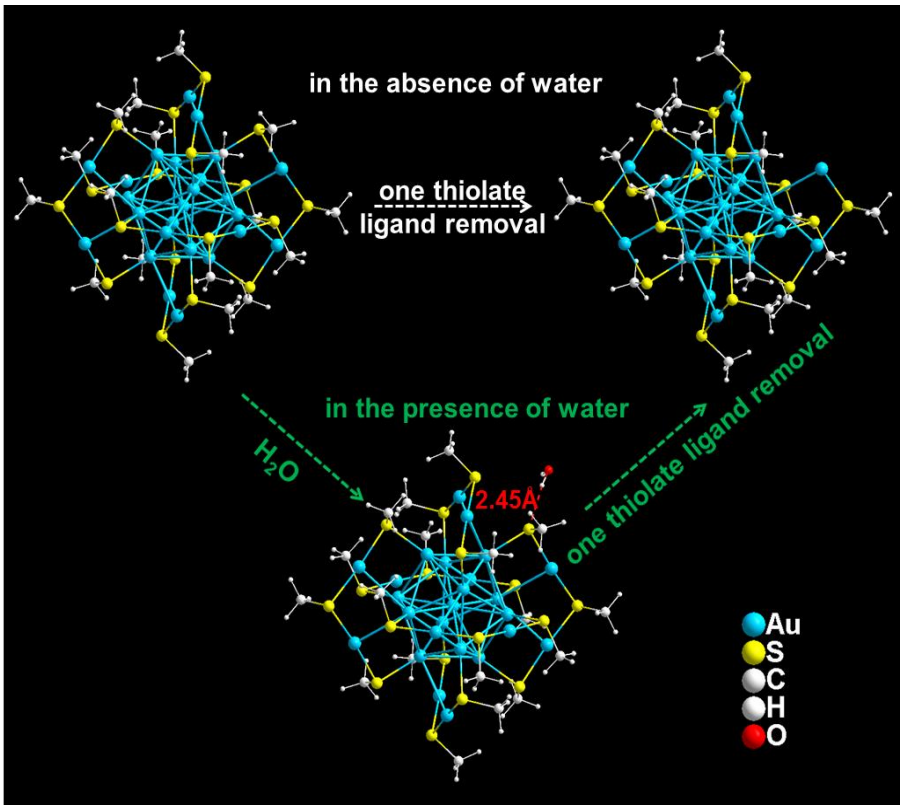

Figure S7. Detachment of one thiolate ligand from the $Au_{25}(SCH_3)_{18}$ model cluster to result in $Au_{25}(SCH_3)_{17}$. The "-SCH_3" ligand removal in the presence of water (down panel) is more favorable by 45.9 kcal/mol than that in the absence of water (upper panel) in gas phase.

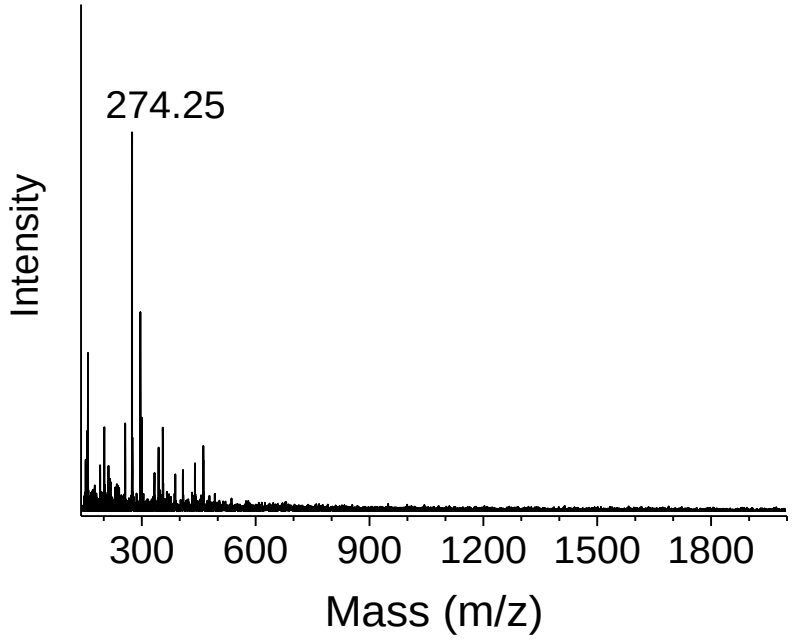

Figure S7. The ESI-MS analysis of the detachment species from the $Au_{25}(SR)_{18}/CeO_2$ in the presence of water and O_2 at 100 ^oC. The strongest mass peak at *m/z* 274.25 (*z* =1) is assigned to R**S**-**S**R.