

Highly-Active Au/ δ -MoC and Au/ β -Mo₂C Catalysts for the Low-Temperature Water Gas Shift Reaction: Effects of the Carbide Metal/Carbon Ratio on the Catalyst Performance

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ADDITIONAL INFORMATION REGARDING COMPUTATIONAL MODELS

Table S1 display the most relevant results for Au₄ clusters supported on the δ -MoC(001) surface. Different adsorption sites have been checked and as one can be seen, the most stable structure (*Cluster 1* and *Cluster 2*) correspond to energy degenerate 3D geometries with three atoms deposited on MMC sites. *Cluster 3* represents a rotated pyramid structure where one Au atom is in contact with Mo surface atoms and the probable repulsion between them provokes the cluster tilt. Eventually, we can consider *Cluster 4* and *5* as 2D, despite of the fact that, as the same case of *Cluster 3*, the Au atoms nearby and/or in contact with Mo surface atoms are located slightly above than atoms in contact with C surface atoms. In conclusion, 3D Au₄ clusters are clearly more stable than 2D.

Table S1: Sketches, relative energies, and adsorption and adhesion energy *per* atom of Au₄ clusters deposited on δ -MoC (001) surface. Mo, C, and Au are denoted by purple, green, and yellow balls, respectively.

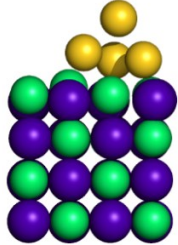
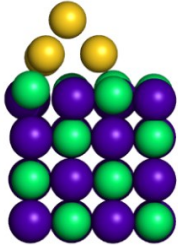
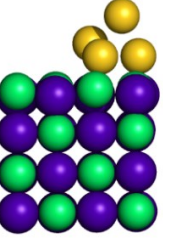
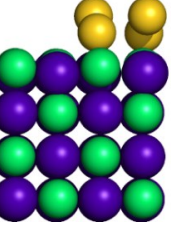
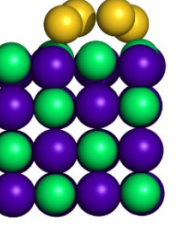
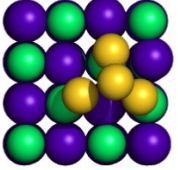
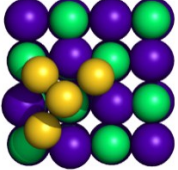
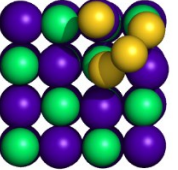
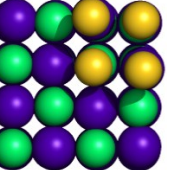
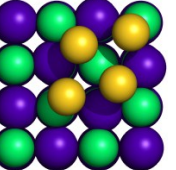
	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
Side view					
Top view					
E _{rel} (eV)	0.00	0.02	0.25	0.45	0.52
E _{ads/atom} (eV)	-1.40	-1.39	-1.34	-1.14	-0.91
E _{adh/atom} (eV)	-1.79	-1.71	-1.68	-1.40	-1.01

Table S2: Energy barriers (eV) of the key steps of the WGS reaction on clean δ -MoC(001) and Au₄/ δ -MoC(001). In bold, the most favorable barrier.

Step	δ -MoC (001)	Au ₄ / δ -MoC (001)
H ₂ O \rightarrow H+OH	0.53	0.79
OH \rightarrow O+H	1.56	1.64
CO+OH \rightarrow COOH	0.89	0.62
COOH \rightarrow CO ₂ +H	0.27	> 1
OH + OH \rightarrow H ₂ O + O	2.22	0.44
CO+O \rightarrow CO ₂	1.54	0.10
H + H \rightarrow H ₂	0.75	1.01
H ₂ desorption	0.46	0.03
CO ₂ desorption	0.85	0.05

Figure S1: Most relevant sketches of adsorption minima of the WGS reaction on clean δ -MoC (001).

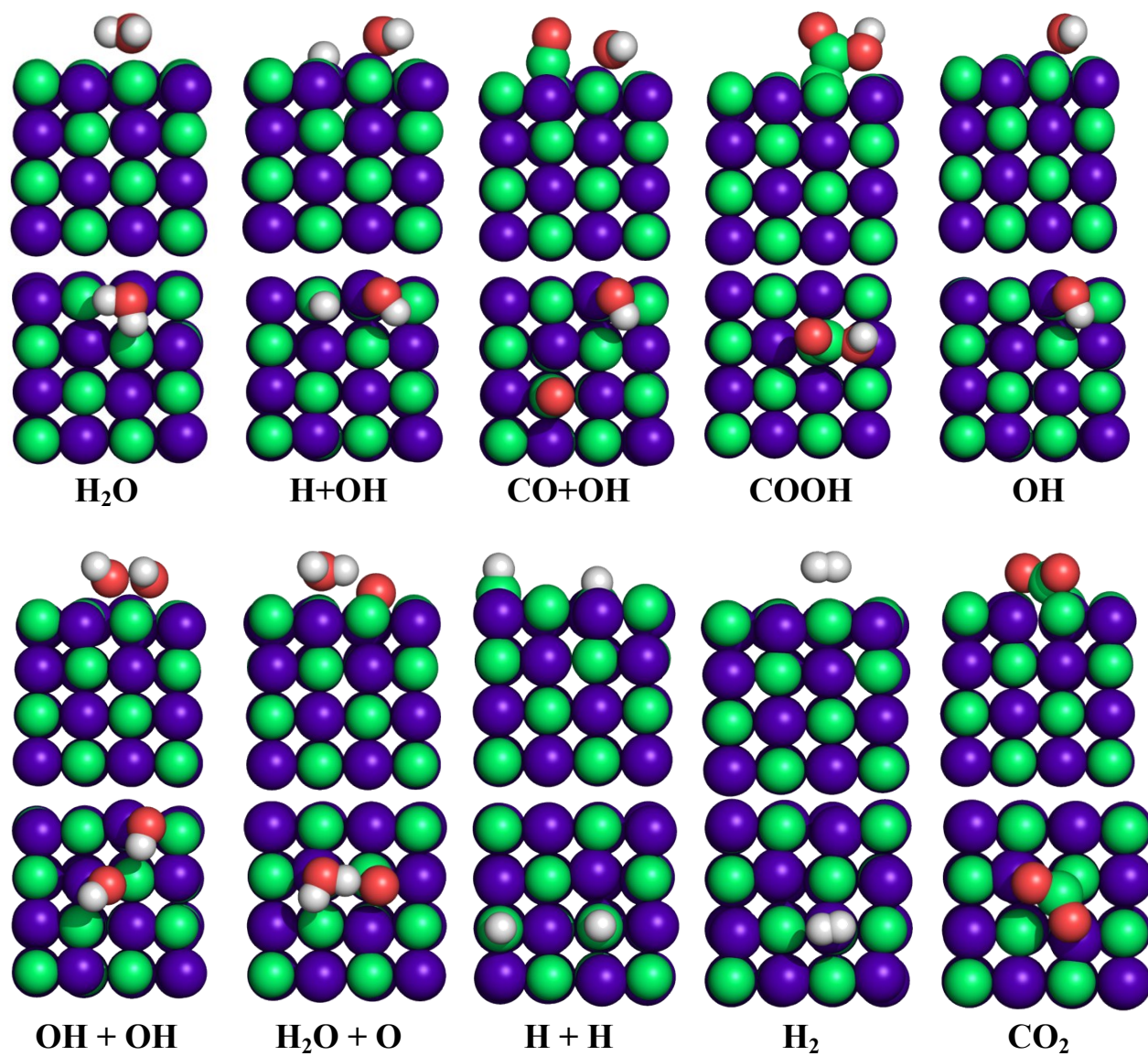


Figure S2: Most relevant sketches of TS structures on clean δ -MoC (001).

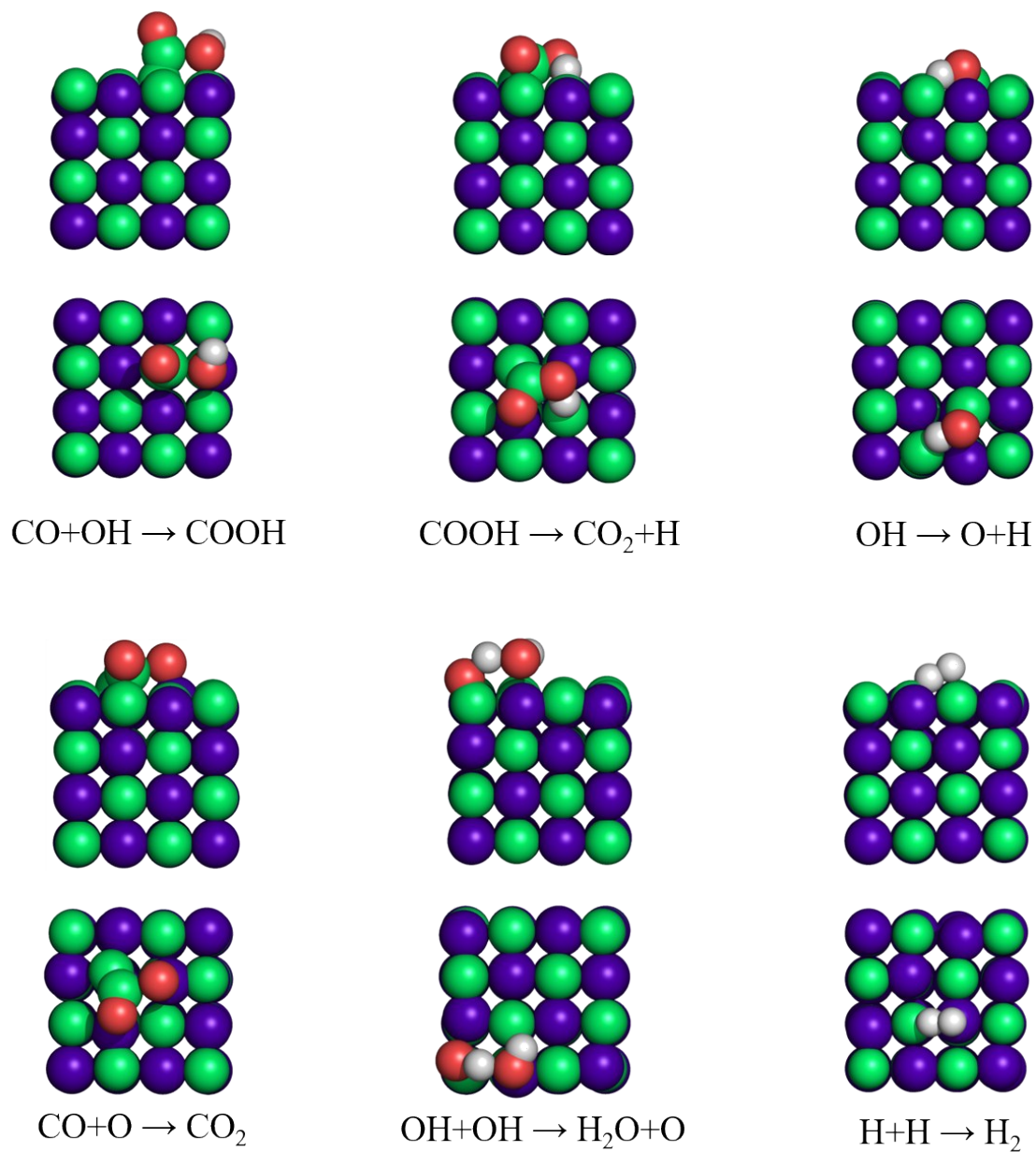


Figure S3: Most relevant sketches of adsorption minima of WGS on Au₄/δ-MoC (001).

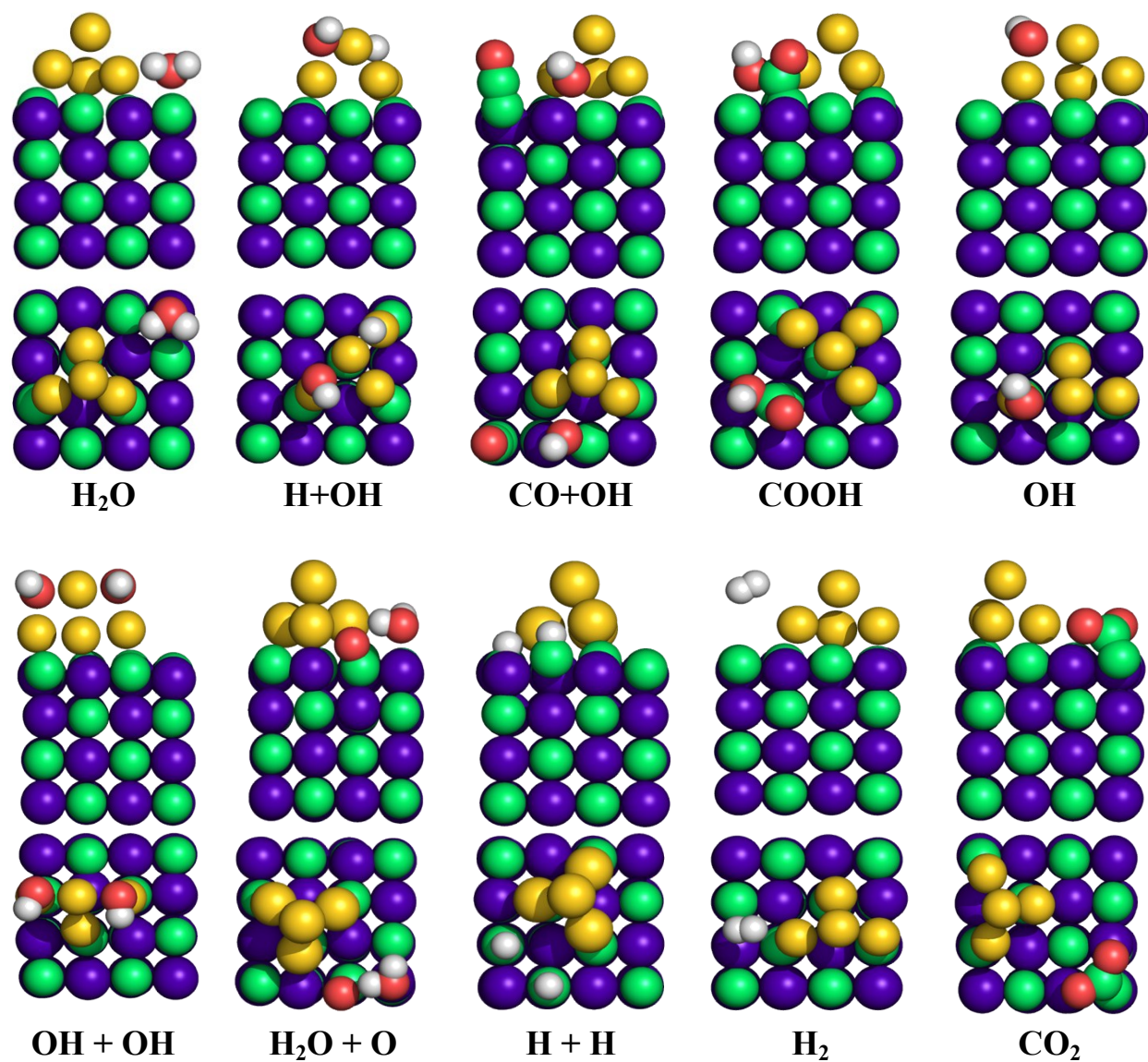


Figure S4: Most relevant sketches of TS structures on Au₄/δ-MoC (001).

