Supporting Information

Exploring Metal-Support Interactions to Immobilize Sub-nm Co Clusters on γ–Mo_2N: A Highly Selective and Stable Catalyst for CO_2 Activation.

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Figures and Tables

Table S1. Physical properties of Co/γ-Mo_2N catalysts

Catalysts	BET surface area (m^2/g)	Cobalt loading (wt%)
γ-Mo_2N	52	-
1% Co/γ-Mo_2N	48	1.35
2% Co/γ-Mo_2N	42	1.96
5% Co/γ-Mo_2N	40	4.80
2% Co/ZrO_2	87	2.12
2% Co/CeO_2	41	1.98

X-ray powder diffraction

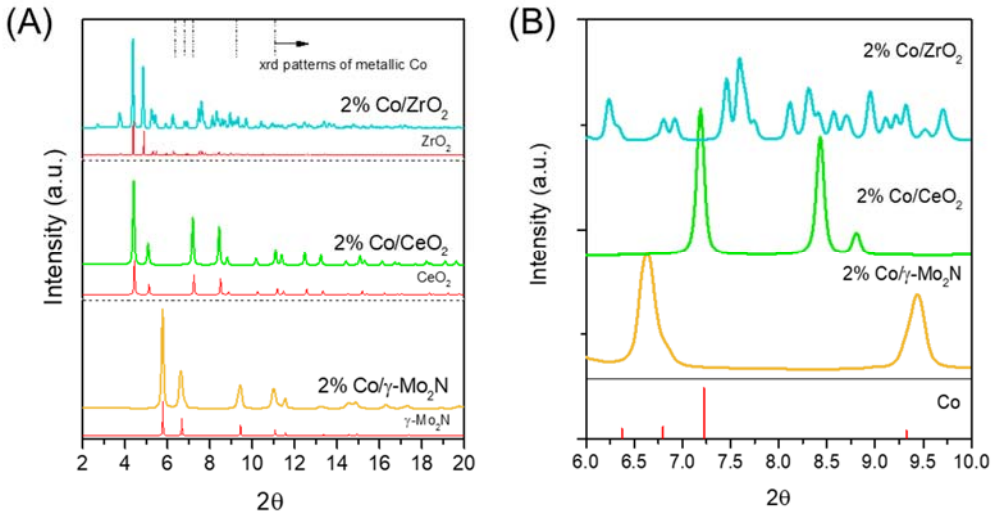


Figure S1. The powder diffraction patterns of (A) the Co/γ-Mo_2N and Co/CeO_2, Co/ZrO_2 reference catalysts. The diffraction pattern of Co is shown in the bottom of the figures. (B) The enlarged profiles of Figure (A) from 6.0 to 10.0 °.

Scanning transmission electron microscopy

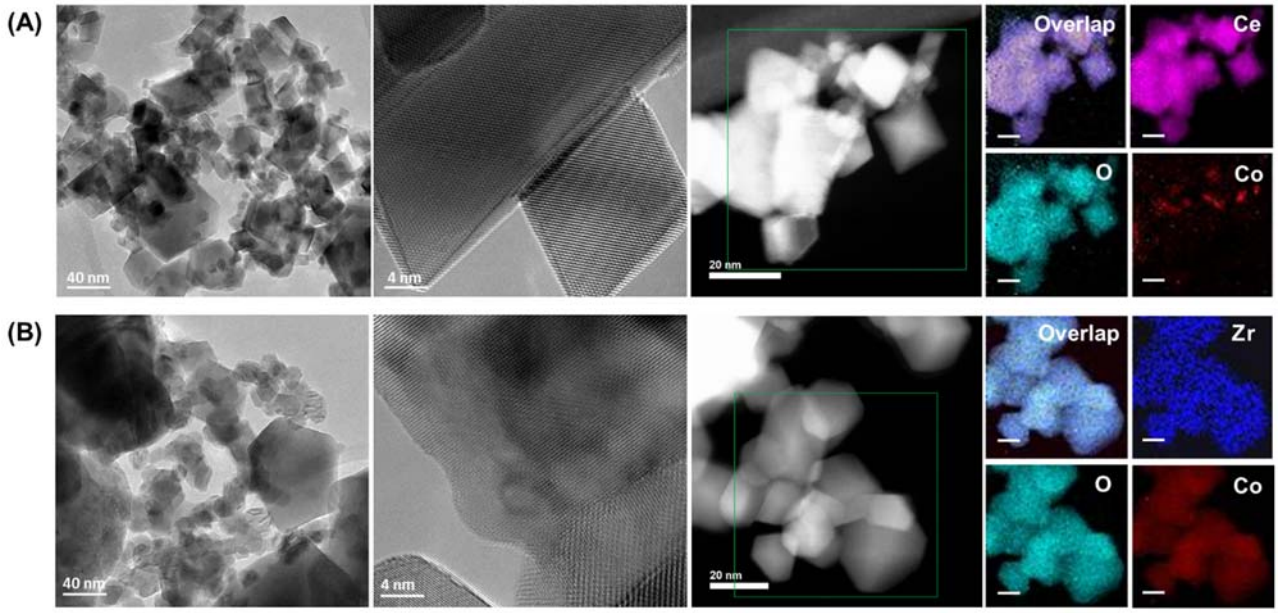


Figure S2. TEM and STEM images of the reference catalysts. (A) 2% Co/CeO_2 and (B) 2% Co/ZrO_2. The scale bar in the EELS mapping equals 10 nm.

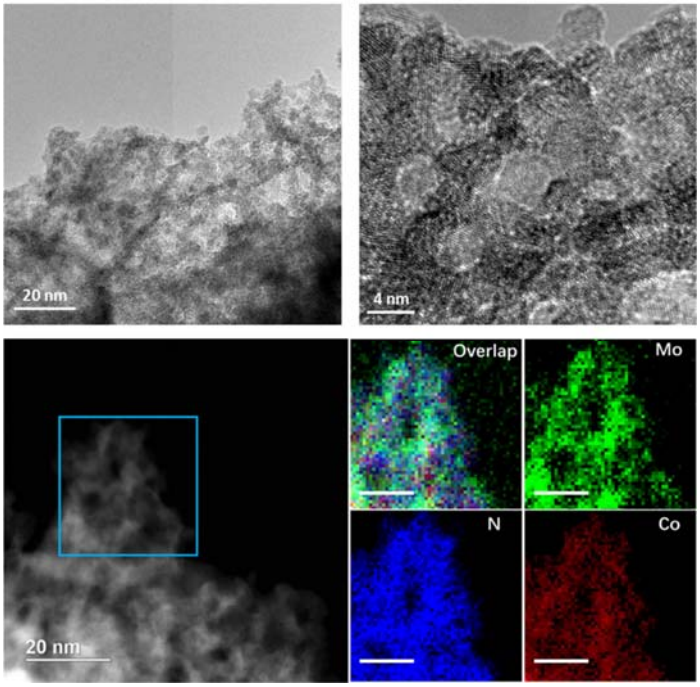


Figure S3. TEM and STEM images and element mapping of the 5% $Co/\gamma\text{-}Mo_2N$ catalyst. The scale bar in the EELS mapping equals 10 nm.

X-ray Absorption Fine Structure Spectroscopy

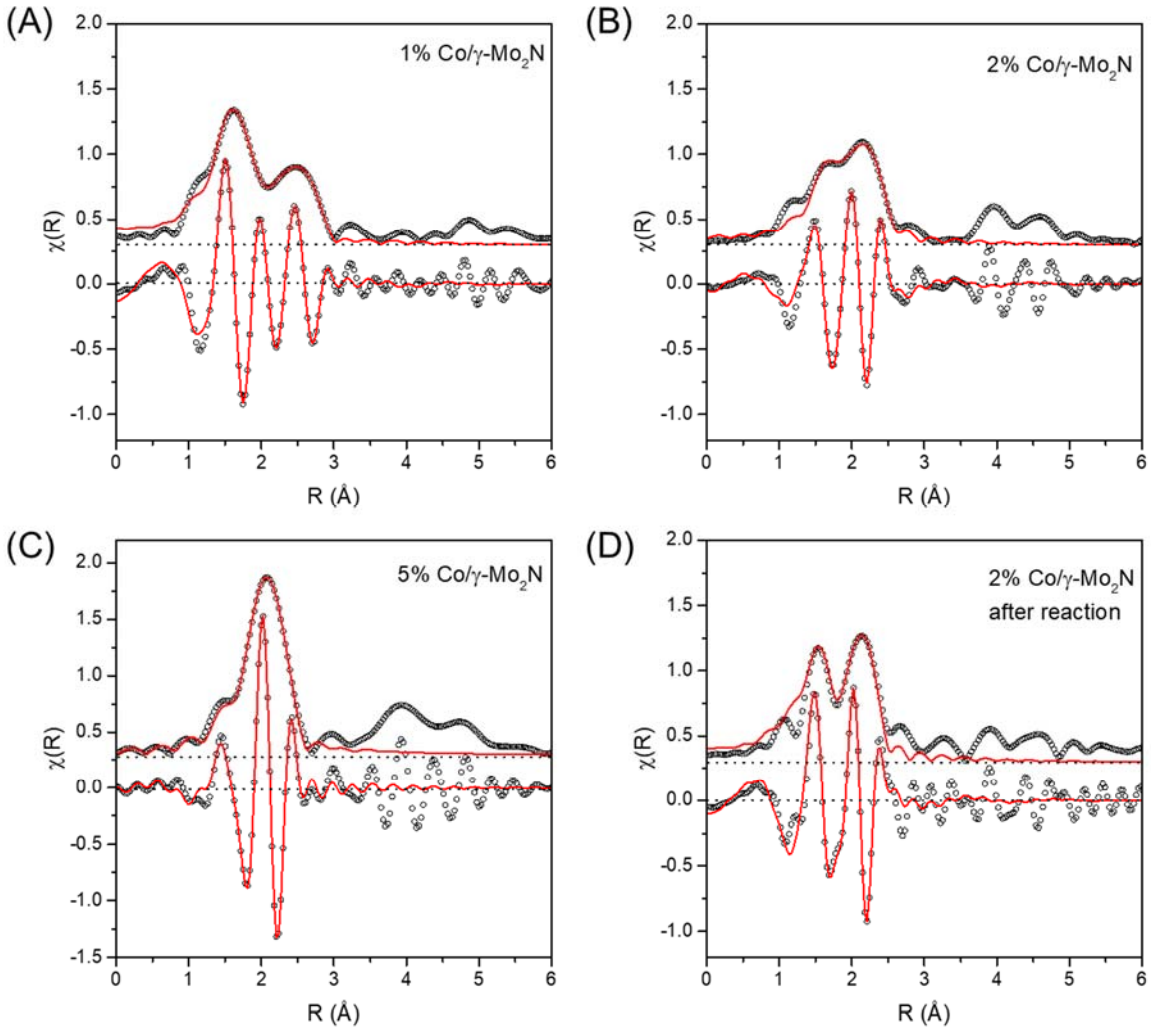


Figure S4. Co K edge EXAFS fitting plots of the tested catalysts in R space. (A) 1% Co/γ-Mo_2N (B) 2% Co/γ-Mo_2N; (C) 5% Co/γ-Mo_2N after reduction; and (D) 2% Co/γ-Mo_2N after reaction

Table S2. Co K edge EXAFS fitting results of Co/γ-Mo_2N catalysts

Entry	Sample	Shell	Bond length (Å)	Coordination Number	σ^2 (Å^2)	E_0 shift (eV)
1	1% Co/γ-Mo_2N	Co-N	2.02±0.01	2.5±0.2	0.003±0.001	2.9
		Co-Co	2.51±0.01	2.4±0.2	0.006±0.001	3.0
		Co-Mo	2.86±0.01	1.3±0.4	0.004±0.001	2.4
2	2% Co/γ-Mo_2N	Co-N	2.02±0.02	1.6±0.2	0.004±0.002	8.0
		Co-Co	2.50±0.01	2.9±0.5	0.007±0.001	0.7
3	5% Co/γ-Mo_2N	Co-N	2.02±0.02	1.2±0.5	0.006±0.002	5.7
		Co-Co	2.49±0.01	4.1±0.5	0.005±0.001	-5.6
4	2% Co/γ-Mo_2N after reaction	Co-N	1.96±0.02	1.6±0.4	0.003±0.001	-5.2
		Co-Co	2.48±0.01	2.4±0.8	0.004±0.001	-2.9
5	2% Co/CeO_2 reduced	Co-Co	2.49±0.02	8.4±0.8	0.006±0.002	-1.1
6	2% Co/ZrO_2 reduced	Co-Co	2.50±0.01	9.1±0.5	0.005±0.002	1.4

Table S3. The comparison of the EXAFS fitting results of the 1% Co/γ-Mo_2N using Co-Mo or Co-O-Co paths

Sample	Shell	Bond length (Å)	Coordination Number	σ^2 (Å^2)	E_0 shift (eV)
1% Co/γ-Mo_2N (Co-Mo)	Co-N	2.02±0.01	2.5±0.2	0.003	3.2
	Co-Co	2.51±0.01	2.4±0.2	0.006	
	Co-Mo	2.86±0.01	1.3±0.4	0.004	
1% Co/γ-Mo_2N (Co-O-Co)	Co-N	2.03±0.01	2.4±0.2	0.003	5.3
	Co-Co	2.53±0.01	3.4±0.4	0.006	
	Co-Co	3.03±0.02	0.5±0.5	-0.002	

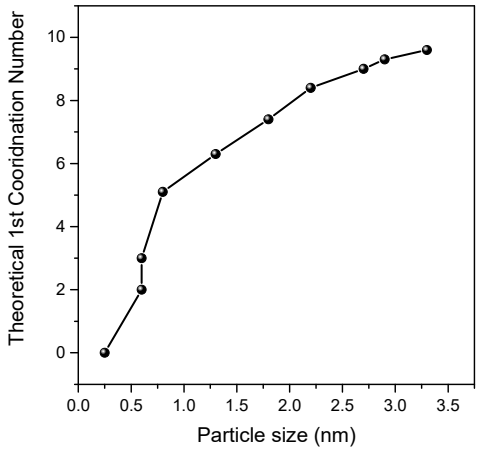
The meaningless fitting parameters were marked in red

The fitting results demonstrate that the Co-O-Co fitting attempt is not reasonable as the σ^2 value is negative and the correspondent C.N. exhibits extremely large fitting error.

Determine the size of the Co clusters based on the EXAFS fitting results

Table S4. The relationship of cluster size and average coordination number of the first nearest neighbor.[1-3]

Clusters/Particles	Size (nm)	Average theoretical 1st Coordination number
M_1	0.25	0
M_3	0.6	2
M_4	0.6	3
M_{10}	0.8	5.1
M_{38}	1.3	6.3
M_{66}	1.8	7.4
M_{138}	2.2	8.4
M_{243}	2.7	9.0
M_{303}	2.9	9.3
M_{476}	3.3	9.6



Based on the relationship of theoretical 1st shell coordination number with the increasing half-sphere particle size, it could be seen that at the small particle size region, the coordination number is very sensitive to the particle size change.

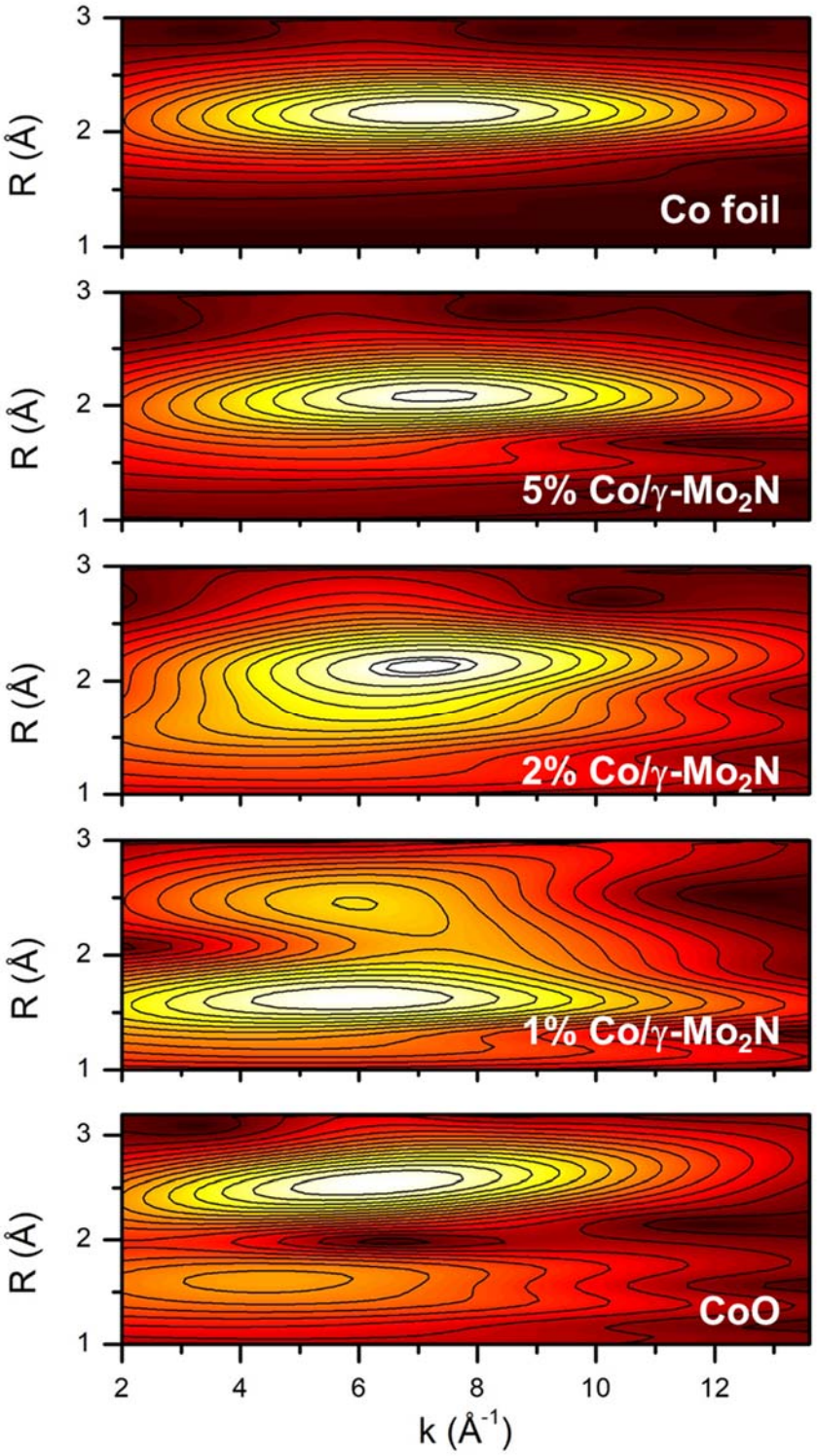


Figure S5. Wavelet Transformation (WT) spectra of activated Co/γ-Mo_2N catalysts.

Justification for the EXAFS fitting (Taking 1% Co/γ-Mo_2N as an example)

The fitting quality of each Co spectra could be seen from the Figure S3. To justify the choice of the structure models, especially the use of Co-Mo rather than Co-O-Co (Co-N-Co) shell in the 1% Co/g-Mo_2N sample, the following information is listed.

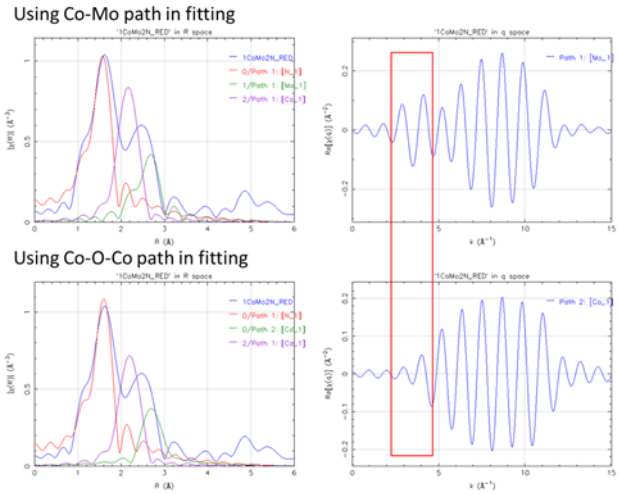


Figure S6. The comparison of the EXAFS fittings of the in R space and q-real space using Co-Mo or Co-O-Co paths.

Only based on the R space spectra, the choice of Co-Mo or Co-O-Co both seems OK. However, it could be noticed that the oscillation of Co-Mo path in the q space shows a local maximum which is absence in the Co-O-Co sample. Therefore, we further analysis the wavelet transformation spectra.

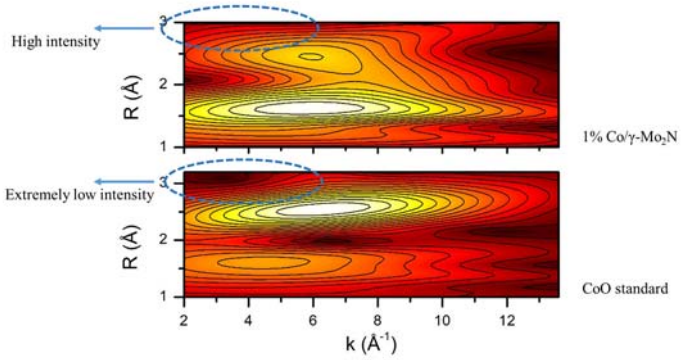


Figure S7. The comparison of the low k part of the WT diagram of the 1% Co/γ-Mo_2N and CoO standard. The blue circles show the evidence that the Co-O-Co path should not be included in the EXAFS fitting.

Based on the figures, it is clearly that the 1% Co/γ-Mo_2N shows considerable intensity in the region of the blue circle, which is different from CoO standard. Therefore, we confirm that the high R component should probably be Co-Mo. The fitting results of the R space spectra will further confirm this conclusion.

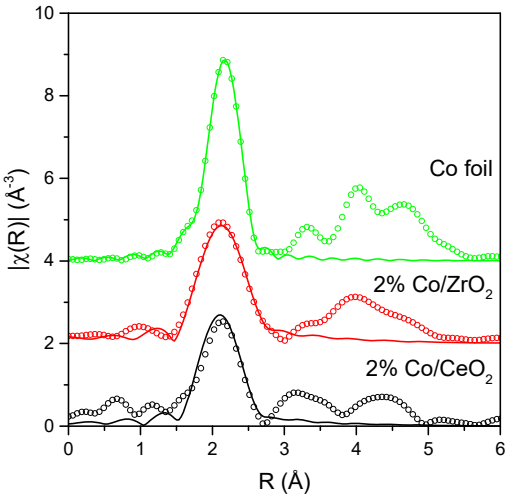


Figure S8. Co K edge EXAFS fitting plots of the reference catalysts in R space.

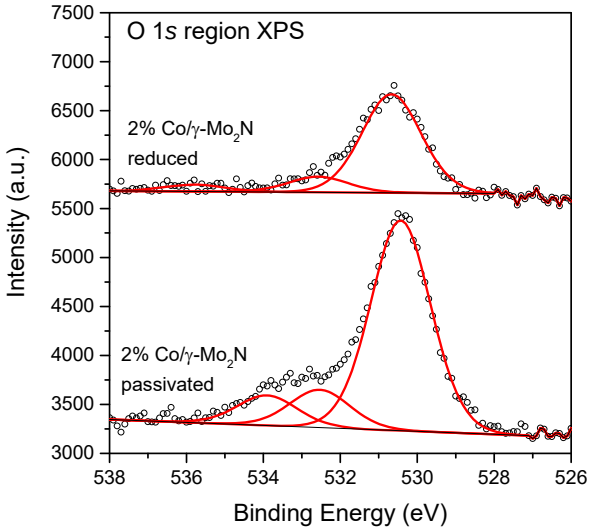


Figure S9. The O 1s XPS spectra of the 2% Co/γ-Mo2N. (A) passivated sample and (B) reduced sample in the AP-XPS chamber (~60% of the oxygen signal was removed). The reduction of the sample was done at 500 °C using only15 mTorr of H_2. A larger reduction is expected upon exposure of the sample to H_2-rich streams at higher temperatures.

Table S5. The peak affiliation of the AP-XPS spectra

Binding Energy (eV)	Species
Mo 3*d* region (The $3d_{5/2}$ and $3d_{3/2}$ split energy is 3.13 eV)	
228.50	Mo nitride
229.23	Mo (IV)
230.44	Mo (V)
232.25	Mo (VI)
Mo 3*p* region (The $3p_{3/2}$ and $3p_{1/2}$ split energy is 17.55 eV)	
394.85	Mo nitride
396.65	Mo (IV)
398.85	Mo(VI)
N 1*s* region	
397.80 eV	Nitride N

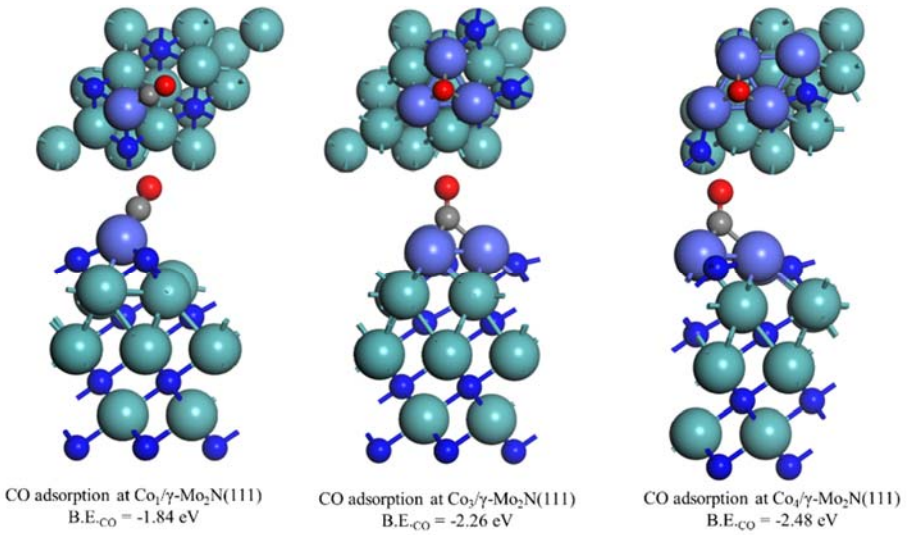


Figure S10. The calculation of the adsorption energy of CO on the Co_1, Co_3 and Co_4/γ-Mo_2N(111) model surfaces.

References

1. Beale, A. M.; Weckhuysen, B. M., *EXAFS as a tool to interrogate the size and shape of mono and bimetallic catalyst nanoparticles*. *Phys. Chem. Chem. Phys.* **2010,** *12*, 5562-5574.
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3. Kibata, T.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K., *Investigation of size-dependent properties of sub-nanometer palladium clusters encapsulated within a polyamine dendrimer*. *Chem Commun* **2013,** *49*, 167-169.