Supporting Information

The interaction of CO molecules on Au-Rh bimetallic nanoclusters supported on a thin film of Al_2O_3/NiAl(100)

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Figure S1 shows TPD spectra of CO (5.0 L) adsorbed as a probe on Au/Rh and Rh/Au bimetallic clusters (1.0 ML Au + 1.0 ML Rh) on Al_2O_3/NiAl(100). The desorption intensities of CO were used as a measure of number of surface sites, as CO adsorbed on atop sites of Rh and low-coordinated Au on the bimetallic clusters. The CO desorption feature at temperature 100 – 300 K resembles closely that from pure Au clusters,[1,2] so is assigned to the desorption of CO from Au sites (CO_{Au}); the desorption feature between 300 and 550 K resembled that from pure Rh clusters,[3] so is ascribed to desorption of CO from Rh sites (CO_{Rh}) of the bimetallic clusters. The results show that for Au/Rh clusters, the desorption signals from CO_{Au} are comparable to those from CO_{Rh}; 1.0-ML Au did not cover entirely 1.0-ML Rh

clusters. For Rh/Au clusters, a similar result was obtained.

We conducted a series of DFT-based simulation to shed light on the effect of CO_{Au} on the IR absorption intensity of CO_{Rh}. We investigate systematically the adsorbate, electronic and structural effects for CO adsorbed on Au and Rh surfaces. To derive adsorption energies (E_{ads}), vibrations (v), bond length ($r_{C=O}$) and charges (q_C and q_O), the optimized adsorption structures are required. Figure S2 shows the optimized adsorption structures of CO_{Au} at varied coverages on the Au(100), Rh/Au(100), Au/Rh(100), Au_{38} and Au_{step} surfaces, and Figure S3 shows those of CO_{Rh} at varied coverages on the Rh(100), Rh/Au(100), Au/Rh(100), Rh_{38} and Rh_{step} surfaces. The corresponding energies (E_{ads}), vibrations (v), bond length ($r_{C=O}$) and charges (q_C and q_O) are listed in Table S1.

References

1. Y. D. Li, T. C. Hong, T. W. Liao and M. F. Luo, *Surface Science*, 2013, **618**, 132-139.
2. S. A. Tenney, J. S. Ratliff, C. C. Roberts, W. He, S. C. Ammal, A. Heyden and D. A. Chen, *The Journal of Physical Chemistry C*, 2010, **114**, 21652-21663
3. T.-C. Hung, T.-W. Liao, Z.-H. Liao, P.-W. Hsu, P.-Y. Cai, W.-H. Lu, J.-H. Wang and M.-F. Luo, *RSC Advances*, 2016, **6**, 3830-3839

Figure S1

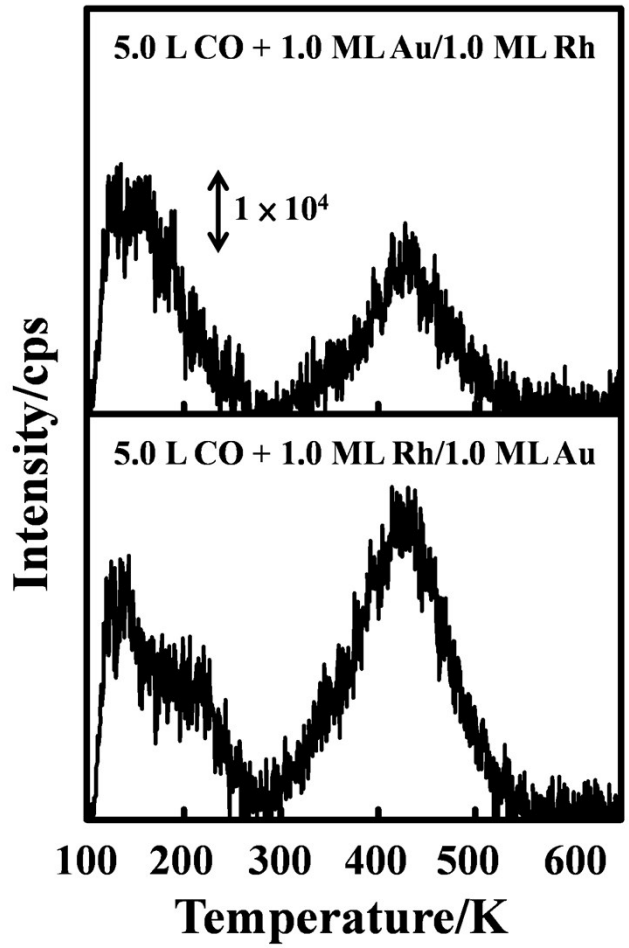

Figure S1 CO TPD spectra for Au/Rh (upper) and Rh/Au (lower) bimetallic clusters on thin-film Al_2O_3/NiAl(100) exposed to CO (5.0 L) at 100 K. The bimetallic clusters were formed on deposition of 1.0 ML Au (Rh) onto pre-deposited 1.0 ML Rh (Au) on the oxide at 300 K. CO at 5.0 L is sufficient to saturate the surface; no CO adsorbed on the oxide at 100 K.

Figure S2

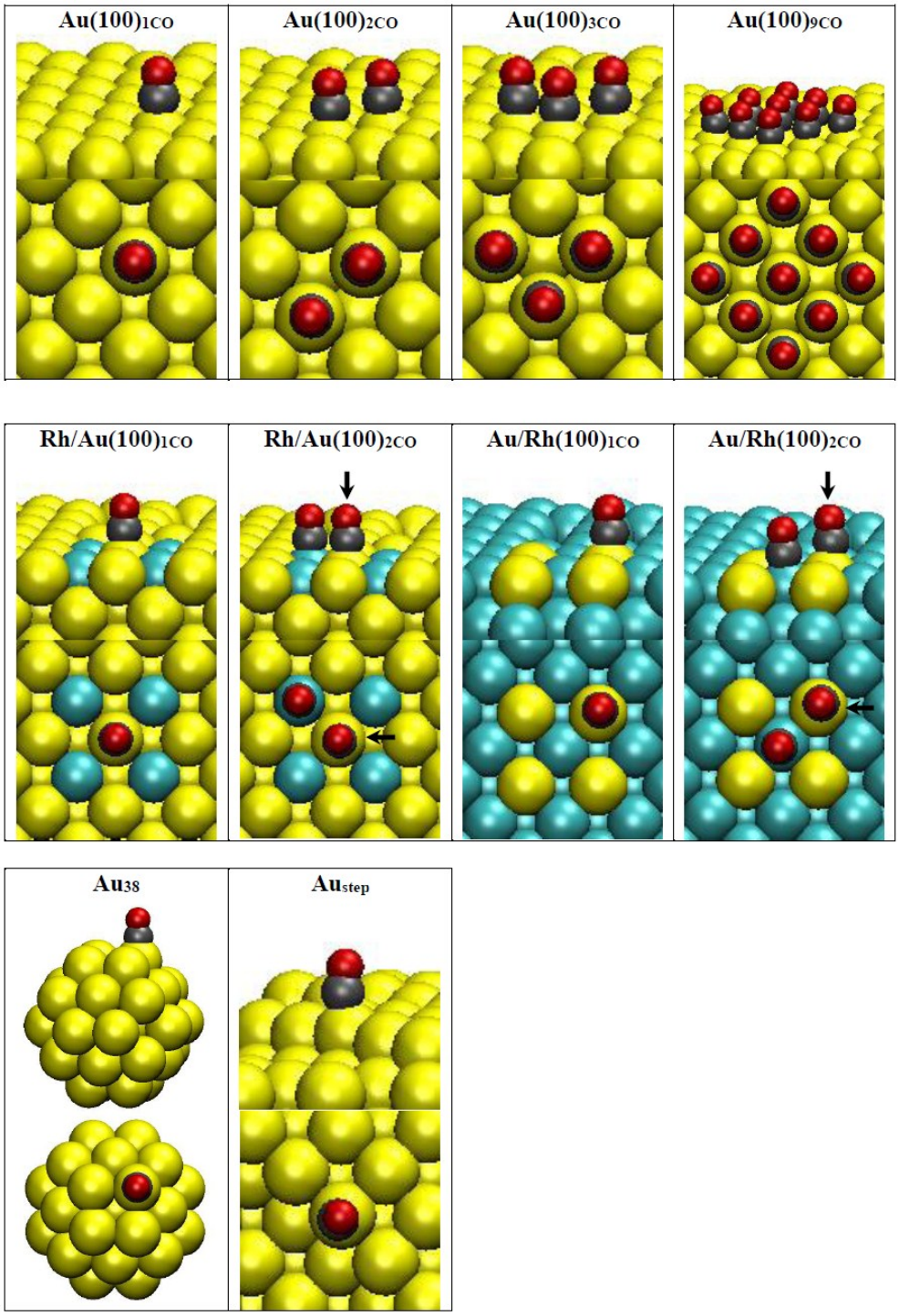

Figure 2S Top and side views of the optimized adsorption structures of CO_{Au} at varied coverages on the Au(100), Rh/Au(100), Au/Rh(100), Au_{38} and Au_{step} surfaces. The Au, Rh, C and O atoms are shown as yellow, cyan, grey and red spheres, respectively.

Figure S3

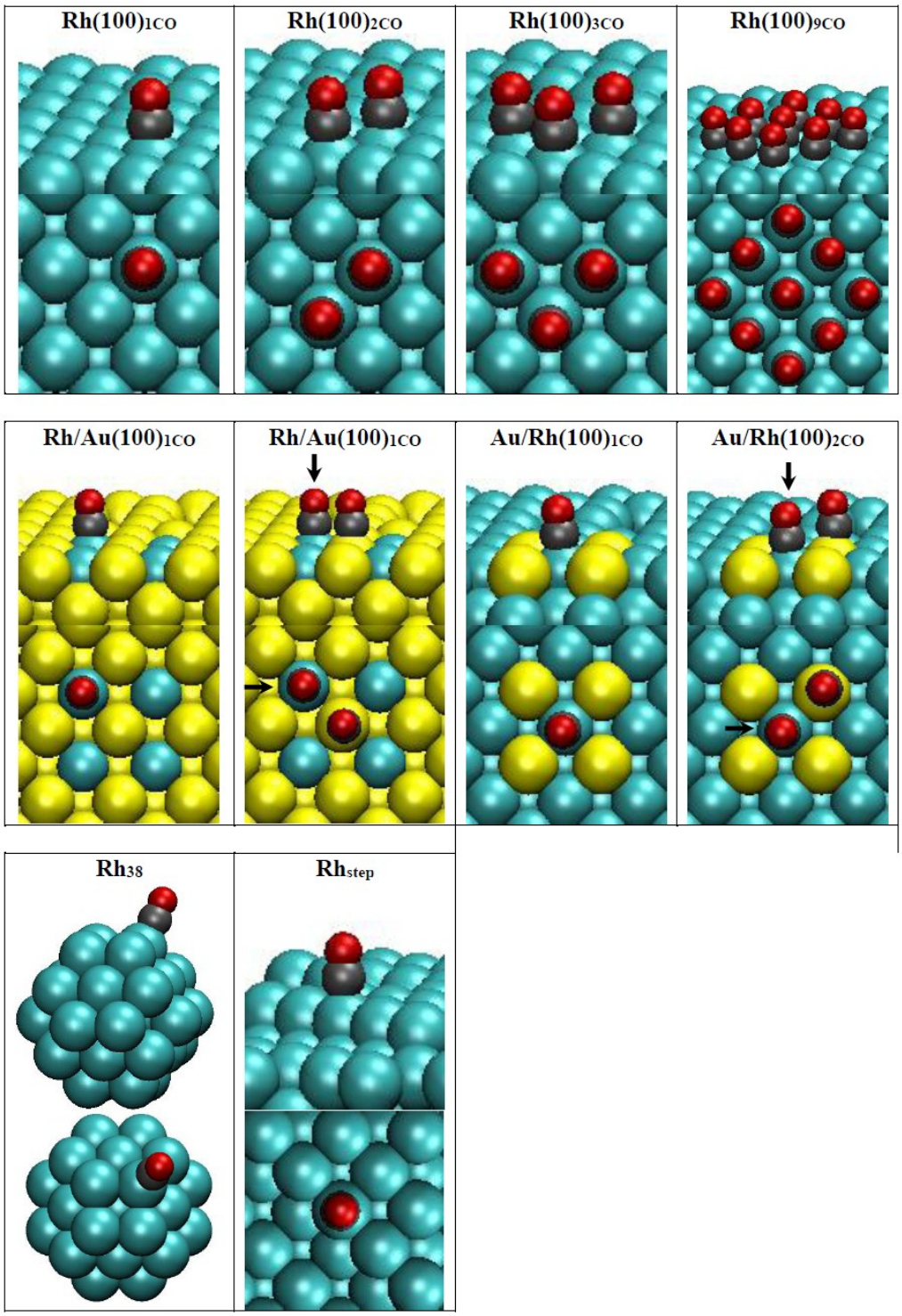

Figure S3 Top and side views of the optimized adsorption structures of CO_{Rh} at varied coverages on the Rh(100), Rh/Au(100), Au/Rh(100), Rh_{38} and Rh_{step} surfaces. The Au, Rh, C and O atoms are shown as yellow, cyan, grey and red spheres, respectively.

Table S1

		CO_{Au}					CO_{Rh}				
		E_{ads}	v	r_{CO}	q_C	q_O	E_{ads}	v	r_{CO}	q_C	q_O
Adsorbate effect	**M(100)$_{1CO}$**	-0.45	2058	1.152	1.85	-1.83	-1.99	2009	1.160	1.54	-1.85
	M(100)$_{2CO}$	-0.45	2060	1.151	1.77	-1.81	-1.94	2014	1.161	1.56	-1.82
	M(100)$_{3CO}$	-0.45	2062	1.151	1.78	-1.81	-1.93	2020	1.161	1.56	-1.81
	M(100)$_{9CO}$	-0.40	2063	1.151	1.80	-1.81	-1.69	2042	1.161	1.58	-1.81
Electronic effect	**Rh/Au(100)$_{1CO}$**	-0.52	2058	1.151	2.01	-1.99	-2.17	2003	1.162	1.75	-2.02
	Rh/Au(100)$_{2CO}$	-0.48	2054	1.151	1.95	-1.96	-2.13	1969	1.167	1.68	-1.98
	Au/Rh(100)$_{1CO}$	-0.50	2050	1.152	1.88	-1.94	-1.85	1993	1.164	1.64	-1.92
	Au/Rh(100)$_{2CO}$	-0.48	2047	1.152	1.90	-1.93	-1.81	1984	1.163	1.60	-1.89
Structural effect	**M$_{step}$**	-0.55	2037	1.152	1.83	-1.85	-2.03	1950	1.169	1.63	-1.88
	M$_{cluster}$	-0.80	2031	1.153	1.83	-1.88	-2.45	1937	1.171	1.61	-1.92

Table S1 The computed adsorption energy (E_{ads}) in eV, vibrational frequency (v) in cm^{-1}, C-O bond length (r_{CO}) in Å and Bader charges (q_C and q_O) in |e| for various CO_{Au} and CO_{Rh}, including **M(100)$_{1CO}$**, **M(100)$_{2CO}$**, **M(100)$_{3CO}$** and **M(100)$_{9CO}$** for the adsorbate effect, **Rh/Au(100)$_{1CO}$**, **Rh/Au(100)$_{2CO}$**, **Au/Rh(100)$_{1CO}$** and **Au/Rh(100)$_{2CO}$** for the electronic effect and **M$_{step}$** and **M$_{cluster}$** for the structural effect.