## Supplementary Information

## Decomposition of methanol- $d_4$ on Au-Rh bimetallic nanoclusters on a thin film of Al<sub>2</sub>O<sub>3</sub>/NiAl(100)

Hsuan Lee,<sup>a</sup> Zhen-He Liao<sup>a</sup>, Po-Wei Hsu<sup>a</sup>, Yu-Cheng Wu<sup>a</sup>, Yuwei Lin<sup>b</sup>, Jeng-Han Wang<sup>b,\*</sup> and Meng-Fan Luo<sup>a,\*</sup>

<sup>a</sup>Department of Physics, National Central University, 300 Jhongda Road, Jhongli 32001, Taiwan <sup>b</sup>Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan

\*Corresponding authors E-mail: <u>mfl28@phy.ncu.edu.tw</u> (M. F. Luo) and jenghan@ntnu.edu.tw (J. H. Wang)

The number of the Rh sites was measured with the integrated intensity of CO TPD spectra from molecularly adsorbed CO on the bimetallic clusters as a probe. CO molecules adsorb linearly on surface Rh, so they can serve as a measure of Rh sites. Figure S1 and S2 show respectively the measured number of Rh sites on the bimetallic clusters, as a function of deposited Au (for Au/Rh bimetallic clusters) or Rh (for Rh/Au bimetallic clusters). The results show that the Rh sites either decreased linearly with deposited Au (Figure S1) or increased linearly with deposited Rh (Figure S2).

We used TPD and IRAS spectra of CO as a probe molecule to monitor the surface compositions of our bimetallic clusters before and after the reaction. The effect of molecularly adsorbed CO on the structures of

our bimetallic clusters had been shown previously to be negligible.<sup>1</sup> Figure S3a shows the CO TPD spectra for 5.0 L CO molecularly adsorbed on Rh(1.0 ML)/Au(1.0 ML) bimetallic clusters (black) and these clusters pre-exposed to 2.0 L CD<sub>3</sub>OD and annealed to 300 K (red). 5.0 L CO was sufficient to saturate the cluster surface; at 300 K, the dehydrogenation of adsorbed methanol-d<sub>4</sub> was completed. The desorption feature between 100 and 300 K is assigned to CO from Au sites and that between 300 and 550 K to CO from Rh sites. These desorption intensities are used to measure the number of surface Au and Rh sites on the bimetallic clusters. We note that after the reaction (red), the desorption intensity from Au sites decreased slightly while that from Rh sites increased slightly, implying that both the Au and Rh sites altered little. The CO IRAS spectra show a consistent picture. Figure S3b shows CO IRAS spectra for 5.0 L CO molecularly adsorbed on Rh(1.0 ML)/Au(1.0 ML) bimetallic clusters (black) and these clusters pre-exposed to 2.0 L CD<sub>3</sub>OD and annealed to 300 K (red). The narrow, intense absorption line centered about 2100 cm<sup>-1</sup> is attributed CO on Au sites of the bimetallic clusters, and the broad feature ranging from 2080 to 1900 cm<sup>-1</sup> to CO on Rh sites. Consistent with the above TPD results, after the reaction (red), the absorption intensity from Au sites decreased slightly while that from Rh sites increased slightly. On annealing the sample to 300 K to remove most CO from Au sites and hence their effect on the CO signals on Rh sites,<sup>1</sup> the absorption intensity from Rh sites after the reaction (red) remained slightly stronger than that before the reaction (black), shown in Figure S3c. These IRAS results suggest also that the surface compositions altered little after the reaction. Such little alternation justifies the present analysis.

The IRAS spectra of C-O stretching, C-D and O-D absorption bands for methanol-d<sub>4</sub> on Rh clusters/Al<sub>2</sub>O<sub>3</sub>/NiAl(100) were recorded to explore the intermediates in the dehydrogenation. Figure S4a displays the IRAS spectra of the C-O stretching and  $\delta_s$ (CD<sub>3</sub>) modes of methanol-d<sub>4</sub> on 1.6-ML Rh clusters on

 $Al_2O_3/NiAl(100)$  heated stepwise. Figure S4b shows the corresponding spectra of for the C-O stretching of CO, the O-D and other C-D absorption modes of methanol-d<sub>4</sub>. As claimed in the main text, the spectral features resemble those from Au-Rh bimetallic clusters.

Table S1 lists the adsorption energies ( $E_{ads}$ ) for CD<sub>3</sub>OD\* and its fragments from the decomposition on Rh/Au and Au/Ru surfaces. The results for those on Rh(100) and Au(100) surfaces are also shown for comparison.<sup>2</sup>

Table S2 lists the exothermic ( $\Delta E$ ) and activation ( $E_a$ ) energies for each step of CD<sub>3</sub>OD\* decomposition toward the formation of CO\* and D\* on Au/Rh and Rh/Au bimetallic surfaces. The results from Rh(100) surface are also shown for comparison.<sup>2</sup>

Table S3 shows the altered charge (Bader charges, |e|) and *d*-band centers (eV) of surface Rh atoms on Rh/Au bimetals (Rh/Au surface, Rh<sub>2</sub>Au<sub>36</sub> and Rh<sub>2</sub>Au<sub>38</sub> clusters) and Au/Rh bimetals (Au/Rh surface, Au<sub>2</sub>Rh<sub>36</sub> and Au<sub>2</sub>Rh<sub>38</sub> clusters). The surface Rh atoms on Rh/Au bimetals are in general more positively charged and have higher *d*-band centers.

Figure S5 shows the models for clean Au/Rh and Rh/Au bimetallic surfaces and adsorbed CD<sub>3</sub>OD\*. The surfaces correspond to the optimized structures of a layer of Au and Rh atoms on the Rh(100) and Au(100) surfaces, respectively. The thermodynamic stability of those structures are also confirmed from the AIMD simulations.<sup>3</sup>

Figure S6 and S7 show optimized structures of initial, transition and final states of each elementary steps of methanol-d<sub>4</sub> decomposition on Au/Ru and Rh/Au bimetallic surfaces, respectively. The corresponding exothermic ( $\Delta E$ ) and activation ( $E_a$ ) energies for these steps are listed in Table S2.

## References

- 1. H. Lee, Z.-H. Liao, P.-W. Hsu, T.-C. Hung, Y.-C. Wu, Y. Lin, J.-H. Wang and M.-F. Luo, *RSC Advances*, 2017, 7, 13362-13371.
- T.-C. Hung, T.-W. Liao, Z.-H. Liao, P.-W. Hsu, P.-Y. Cai, H. Lee, Y.-L. Lai, Y.-J. Hsu, H.-Y. Chen, J.-H. Wang and M.-F. Luo, ACS Catalysis, 2015, 5, 4276-4287.
- Po-Wei Hsu, Zhen-He Liao, Ting-Chieh Hung, Hsuan Lee, Yu-Cheng Wu, Yu-Ling Lai, Yao-Jane Hsu, Yuwei Lin, Jeng-Han Wang and Meng-Fan Luo, Physical Chemistry Chemical Physics 2017, 19, 14566-14579.



**Figure S1** plot of the integrated intensities of CO desorption spectra from Rh sites of Au/Rh bimetallic clusters on thin-film  $Al_2O_3/NiAl$  (100) exposed to CO (2.0 L) at 100 K. The bimetallic clusters were formed on deposition of Au at 0.25, 0.5, 1.0 and 2.0 ML onto pre-deposited 1.0-ML Rh clusters on the oxide at 300 K. CO at 2.0 L is sufficient to saturate the surface; no CO adsorbed on the oxide at 100 K.



**Figure S2** plot of the integrated intensities of CO desorption spectra from Rh sites of Rh/Au bimetallic clusters on thin-film  $Al_2O_3/NiAl$  (100) exposed to CO (2.0 L) at 100 K. The bimetallic clusters were formed on deposition of Rh at 0.25, 0.5, 1.0 and 2.0 ML onto pre-deposited 1.0-ML Au clusters on the oxide at 300 K. CO at 2.0 L is sufficient to saturate the surface; no CO adsorbed on the oxide at 100 K.



**Figure S3** shows the CO (a) TPD and (b) IRAS spectra for 5.0 L CO molecularly adsorbed on Rh(1.0 ML)/Au(1.0 ML) bimetallic clusters (black) and these clusters pre-exposed to 2.0 L CD<sub>3</sub>OD and annealed to 300 K (red). (c) IRAS spectra for the same samples annealed to 300 K to remove most CO from Au sites and hence their effect on the CO signals on Rh sites.<sup>1</sup> The bimetallic clusters were grown on deposition of Au (1.0 ML) and subsequently Rh (1.0 ML) on thin-film Al<sub>2</sub>O<sub>3</sub>/NiAl(100) at 300 K. CO and CD<sub>3</sub>OD were adsorbed on the sample at 100 K.



**Figure S4** (a),(b) IRAS spectra of C-O stretching, C-D and O-D absorption modes for 2.0-L CD<sub>3</sub>OD adsorbed on as-prepared (300 K)1.6-ML Rh clusters/Al<sub>2</sub>O<sub>3</sub>/NiAl(100) at 110 K and annealed to selected temperatures. Each spectrum was recorded when the surface was cooled to 110 K after annealing to the indicated temperature.

Table S1: Eads, in eV, of CD<sub>3</sub>OD\* and its fragments on Rh/Au and Au/Ru surfaces, compared to those on

	CD <sub>3</sub> OD*	$CD_3O*$	$CD_2O^*$	CDO*	CO*	$CD_2OD*$	CDOD*	COD*	D*
Au/Rh	-0.30	-2.63	-0.68	-2.50	-1.89	-1.81	-3.28	-5.34	-3.70
Rh/Au	-0.41	-3.14	-1.50	-3.02	-2.23	-2.91	-4.15	-5.97	-3.75
Rh(100) <sup>1</sup>	-0.32	-2.69	-0.71	-2.52	-1.99	-2.06	-3.41	-5.42	-3.74
Au(100)	-0.10	-1.78	-0.08	-1.59	-0.56	-1.61	-2.42	-3.76	-3.22

Rh(100) and Au(100) surfaces.

<sup>1</sup> ref: ACS Catal. (2015) **5** 4276-4289

**Table S2:**  $\Delta E$  and  $E_a$ , in eV, of CD<sub>3</sub>OD\* decomposition toward the formation of CO\* and D\* on Au/Rh and Rh/Au bimetallic surfaces, compared to those on pure Rh(100) surface. The optimized structures are shown in Figures S5 and S6.

		Au/Rh	Rh/Au	Rh(100) <sup>1</sup>
<b>P1.</b> CD OD* $\rightarrow$ CD O* $\perp$ D*	$\Delta E$	-0.17	-0.41	-0.25
<b>KI:</b> $CD_3OD^* \rightarrow CD_3O^* + D^*$	$E_a$	0.55	0.34	0.56
<b>D3.</b> CD $O* \rightarrow CD O* + D*$	$\Delta E$	0.18	-0.16	0.07
<b>K2:</b> $CD_3O^+ \rightarrow CD_2O^+ + D^+$	$E_a$	0.90	0.81	0.91
<b>D3.</b> CD $O* \rightarrow CDO* + D*$	$\Delta E$	-0.31	-0.21	-0.36
<b>K3:</b> $CD_2O^+ \rightarrow CDO^+ + D^-$	$E_a$	0.45	0.38	0.44
<b>D4.</b> CDO* $\rightarrow$ CO* $\perp$ D*	$\Delta E$	-1.24	-0.92	-1.38
<b>K4:</b> $CDO^{+} = CO^{+} + D^{+}$	$E_a$	0.22	0.10	0.20
<b>D5.</b> CD OD* $\rightarrow$ CD OD* $\pm$ D*	$\Delta E$	-0.17	-0.41	0.12
<b>K3:</b> $CD_3OD^+ \rightarrow CD_2OD^+ + D^+$	$E_a$	1.10	1.12	1.05
$\mathbf{D}_{\mathbf{C}}$ CD OD* $\rightarrow$ CDOD* $\perp$ D*	$\Delta E$	-0.05	-0.12	-0.43
<b>K0:</b> $CD_2OD^{+}$ <b>-7</b> $CDOD^{+}$ + D <sup>+</sup>	$E_a$	0.36	0.38	0.34
<b>D7.</b> CDOD* $\rightarrow$ COD* $\perp$ D*	$\Delta E$	-0.24	-0.20	-0.57
$\mathbf{K}$ : $\mathbf{C}$ $\mathbf{D}$ $\mathbf{D}$ $\mathbf{D}$ $\mathbf{T}$ $\mathbf{T}$ $\mathbf{D}$ $\mathbf{T}$		0.50	0.40	0.46
<b>D9.</b> $\Box \Box T = T = T$	$\Delta E$	-0.19	-0.19	-1.27
$\mathbf{N0}: \mathbf{COD}^{*} \rightarrow \mathbf{CO}^{*} + \mathbf{D}^{*}$		0.42	0.35	0.39

<sup>1</sup> ref: ACS Catal. (2015) **5** 4276-4289

**Table S3:** Analyses of altered charge (Bader charge, |e|) and *d*-band centers (eV) of surface Rh atoms on Rh/Au bimetals (Rh/Au surface, Rh<sub>2</sub>Au<sub>36</sub> and Rh<sub>2</sub>Au<sub>38</sub> clusters) and Au/Rh bimetals (Au/Rh surface, Au<sub>2</sub>Rh<sub>36</sub> and Au<sub>2</sub>Rh<sub>38</sub> clusters).

	Bader	<i>d</i> -band center
	charge	
Rh/Au surface	0.09	-1.85
Rh <sub>2</sub> Au <sub>36</sub> cluster	0.18	-1.69
Rh <sub>2</sub> Au <sub>38</sub> cluster	0.20	-1.61
Au/Rh surface	0.05	-2.14
Au <sub>2</sub> Rh <sub>36</sub> cluster	0.06	-2.03
Au <sub>2</sub> Rh <sub>38</sub> cluster	0.03	-2.08



Figure S5. Clean and  $CD_3OD^*$  adsorbed surfaces of Au/Rh and Rh/Au bimetallic models. The surfaces correspond to the optimized structures of a layer of Au and Rh atoms on the Rh(100) and Au(100) surfaces,

respectively.

Figure S6 Optimized structures of initial, transition and final states of each elementary steps of methanol-d<sub>4</sub> decomposition on Au/Ru bimetallic surfaces. Yellow,

cyan, gray, red and white spheres represent as Au, Rh, C, O and D atoms, respectively.





Figure S7 Optimized structures of initial, transition and final states of each elementary steps of methanol-d<sub>4</sub> decomposition on Au/Ru bimetallic surfaces. Yellow,

cyan, gray, red and white spheres represent as Au, Rh, C, O and D atoms, respectively.



