

## Supplementary Information

### **Promoted Activity of Annealed Rh Nanoclusters on Thin Films Al<sub>2</sub>O<sub>3</sub>/NiAl(100) in the Dehydrogenation of Methanol-d<sub>4</sub>**

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Table S1 shows the comparison of diameters and lattice parameters of as-prepared (300 K) and annealed (700 K) Rh clusters at varied coverages (0.5 - 4.0 ML) on Al<sub>2</sub>O<sub>3</sub>/NiAl(100). Modulated reflection rods from NiAl or alumina films, largely due to a roughening oxide surface, are also indicated in the table; they were evident only for Rh coverages  $\geq 3.0$  ML.

Figure S1 compares D<sub>2</sub> TPD spectra from 2.0-L CD<sub>3</sub>OD adsorbed on Rh clusters/Al<sub>2</sub>O<sub>3</sub>/NiAl(100) as prepared (at 300 K) and annealed (700 K). The major desorption feature shifted from about 340 to 480 K, despite of the Rh coverages varying from 0.2 to 2.8 ML. The shift to higher temperature implies the alteration in the surface sites; new surface sites having a stronger bonding with D formed after the sample was annealed to 700 K. Moreover, for 2.8 ML, the integrated intensity of D<sub>2</sub> desorption from the annealed clusters was evidently greater than that from the as-prepared ones, even though the surface sites on the annealed ones were no more than those on the as-prepared ones, indicating that the production of D<sub>2</sub> per surface site on the annealed clusters, the measure of the cluster's reactivity, was enhanced.

Figure S2 compares the production of CO<sub>m</sub> and D<sub>2</sub> per surface Rh site from 2.0-L CD<sub>3</sub>OD on Rh clusters/Al<sub>2</sub>O<sub>3</sub>/NiAl(100) as prepared (300 K) and annealed (700 K). The number of surface Rh sites corresponds to the surface area of the Rh clusters measured with STM. The production of either CO<sub>m</sub> or D<sub>2</sub> per surface Rh site is enhanced at least by two times on the annealed clusters at varied coverages. The result is consistent with that obtained by measuring the number of surface Rh sites with molecularly adsorbed CO.

The IRAS spectra of C-O stretching, C-D and O-D absorption bands for methanol-d<sub>4</sub> on Rh clusters on Al<sub>2</sub>O<sub>3</sub>/NiAl(100) were recorded to explore the intermediates in the dehydrogenation. Figure S3a displays the IRAS spectra of the C-O stretching and  $\delta_s(\text{CD}_3)$  modes of methanol-d<sub>4</sub> on 1.6-ML Rh clusters on Al<sub>2</sub>O<sub>3</sub>/NiAl(100) heated stepwise. Figure S3b 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 resembled those from annealed Rh clusters. Except the O-D bond scission, which was not clear through the IRAS spectra, the other characteristic reaction processes on Rh clusters both as prepared and annealed differed little.

**Table S1**

	0.5 ML Rh	1.0 ML Rh	1.6 ML Rh	4.0 ML Rh
Mean diameter of clusters as prepared	1.4 nm	1.7 nm	2.3 nm	3.5 nm
Mean diameter of clusters annealed*	1.1 nm	1.6 nm	2.2 nm	3.7 nm
Modulated reflection rods after annealing	no	no	no	Yes
Lattice parameter before annealing**	Cannot be resolved	4.04 Å	4.01 Å	3.92 Å
Lattice parameter after annealing	Cannot be resolved	4.02 Å	3.93 Å	3.86 Å

\* Annealing temperature 700 K; \*\* the clusters have an fcc structure.

**Table S1** Comparison of diameters and lattice constants of Rh clusters on Al<sub>2</sub>O<sub>3</sub>/NiAl(100) as prepared (300 K) and annealed (700 K). Modulated reflection rods from NiAl or alumina films, reflecting a roughening oxide surface, are also compared for varied Rh coverages; they are evident only for Rh coverages  $\geq 3.0$  ML.

Figure S1

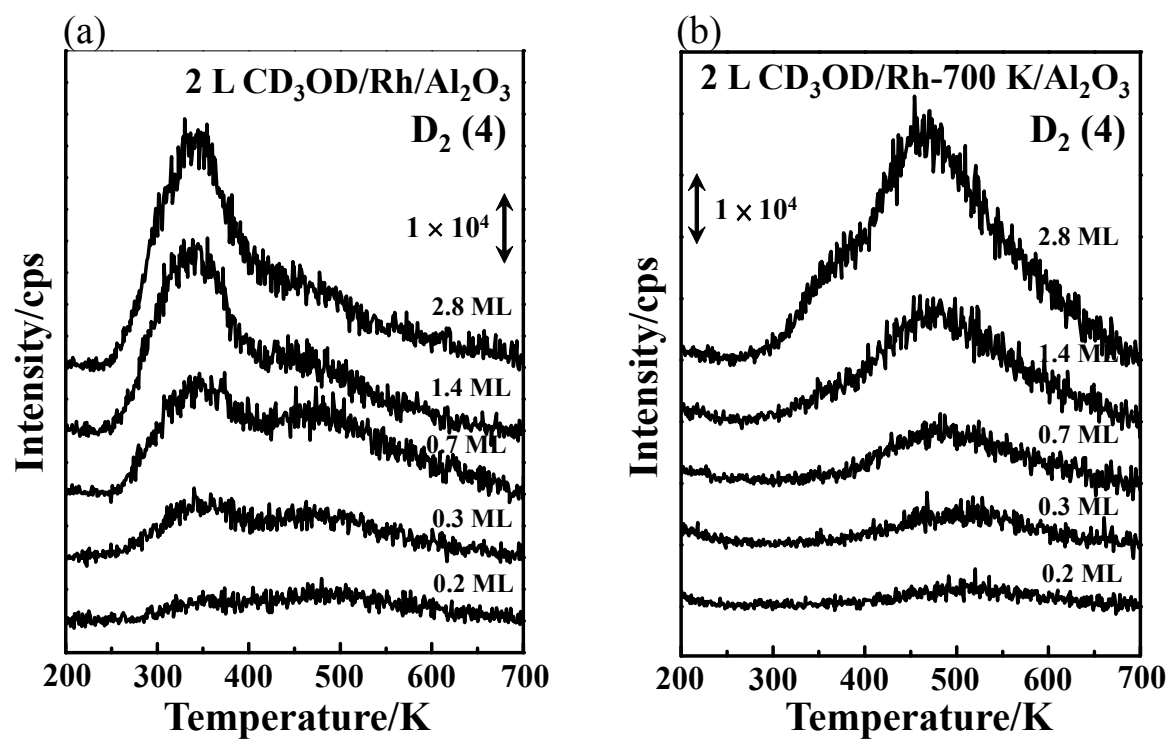
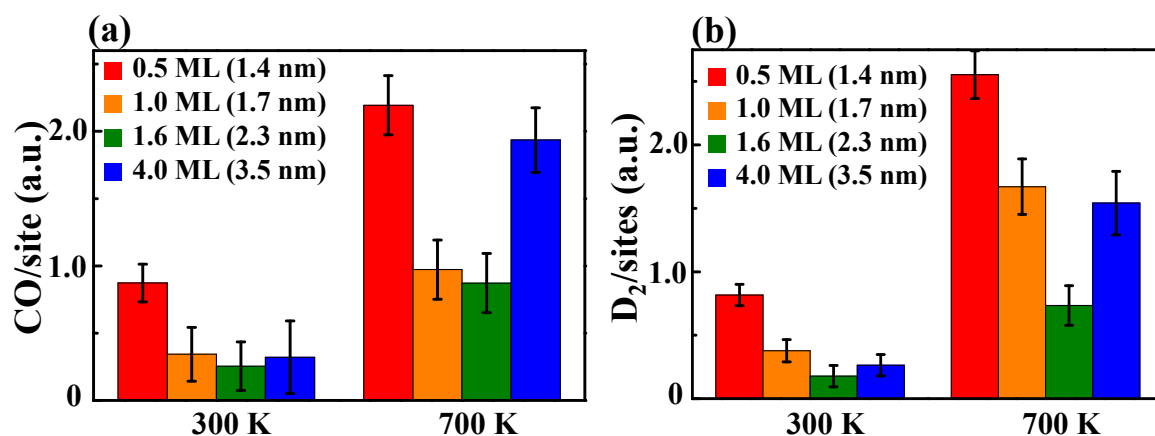


Figure S1 TPD spectra of  $D_2$  ( $m/z = 4$  u) from 2.0-L  $CD_3OD$  adsorbed on Rh clusters/ $Al_2O_3$ /NiAl(100), of varied coverages as indicated, (a) as prepared at 300 K and (b) annealed to 700 K.

Figure S2



**Figure S2** Production of (a) CO<sub>m</sub> and (b) D<sub>2</sub> per surface Rh site from 2.0-L CD<sub>3</sub>OD on Rh clusters/Al<sub>2</sub>O<sub>3</sub>/NiAl(100), of varied coverages (diameters) as indicated, as prepared (300 K) and annealed (700 K). The quantities of the produced CO<sub>m</sub> and D<sub>2</sub> were measured as the integrated intensities of CO and D<sub>2</sub> TPD spectra and the number of surface Rh sites by the surface area of the Rh clusters characterized with STM.

Figure S3

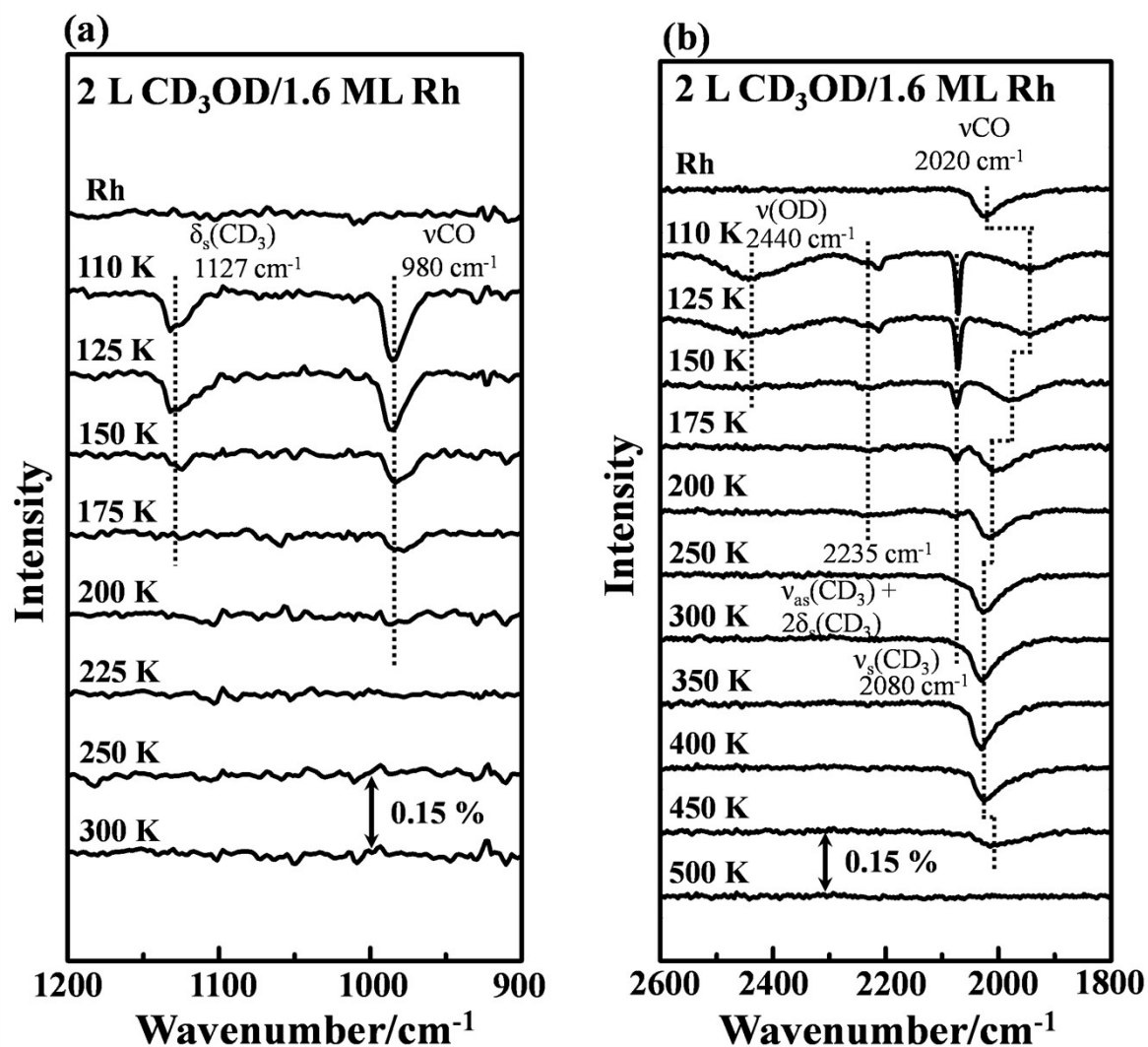


Figure S3 (a),(b) IRAS spectra of C-O stretching, C-D and O-D absorption modes for 2.0-L CD<sub>3</sub>OD adsorbed on as-prepared (300 K) 1.6-ML Rh clusters/Al<sub>2</sub>O<sub>3</sub>/NiAl(100) at 110 K and annealed to selected temperatures. Each spectrum was recorded when the surface was cooled to 110 K after annealing to the indicated temperature.

