Supplementary Information

Designing a Rh-based bimetallic catalyst for heterogeneous ethylene hydroformylation: Combing theoretical predictions and experimental screening

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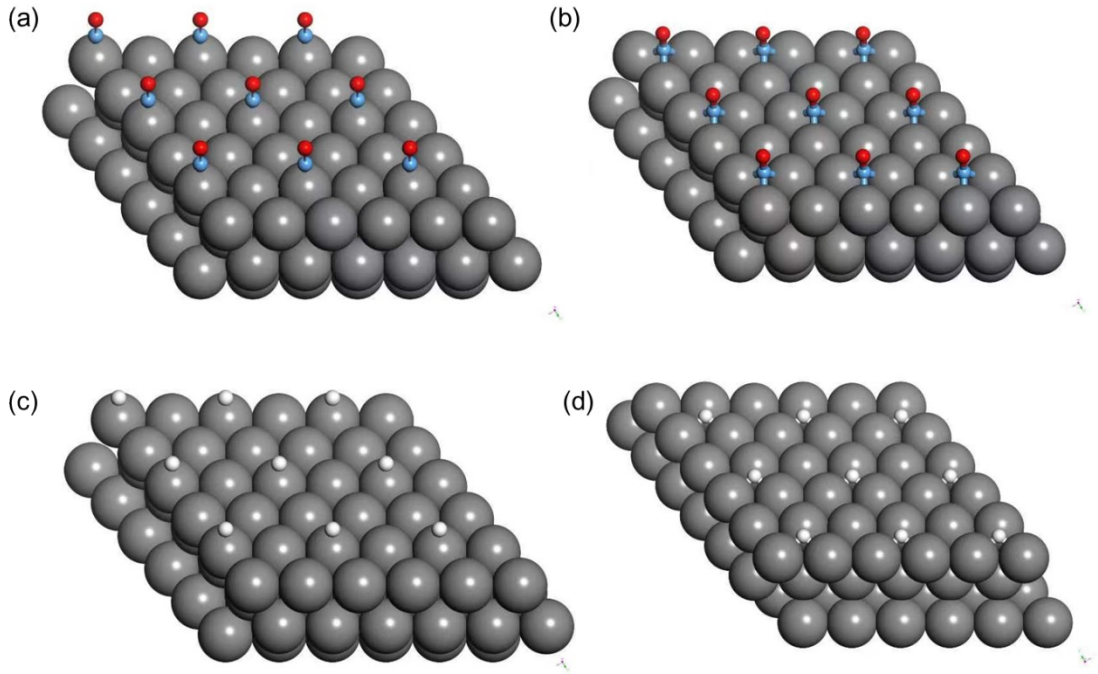

Fig. S1. Configurations of CO on (a) top and (b) hollow sites and H on (c) top and (d) hollow sites of Rh (111) surface. Atom color codes: Rh (grey), C (blue), O (red) and H (white).

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Table S1. CO adsorption energy (E_{ads-CO}) on different surfaces by DFT calculations

Surface	E_{ads-CO} on top site (eV)	E_{ads-CO} on hollow site (eV)
Rh	-2.02	-2.20
RhFe	-2.17	-2.04
RhCo	-2.14	-2.18
RhNi	-2.11	-2.17
RhCu	-2.14	-1.88
RhZn	-2.24	-1.34

Table S2. H adsorption energy (E_{ads-H}) on different surfaces by DFT calculations

Surface	E_{ads-H} on top site (eV)	E_{ads-H} on hollow site (eV)
Rh	-0.22	-0.59
RhFe	-0.30	-0.53
RhCo	-0.25	-0.56
RhNi	-0.25	-0.58
RhCu	-0.27	-0.52
RhZn	-0.38	-0.58

Table S3. Performance of the catalysts in ethylene hydroformylation.

Catalyst	Ethylene conversion (%)	Yield (%)				Oxy selectivity[b] (%)
		Propanal	Propanol[a]	Total oxo[b]	Ethane	
Rh/SiO_2	4.95	1.92	0.60	2.52	2.97	40.2
$RhFe/SiO_2$	7.60	2.08	1.76	3.84	3.76	50.6
$RhCo/SiO_2$	14.8	7.46	0.31	7.77	7.03	52.7
$RhNi/SiO_2$	14.0	4.61	0.14	4.75	9.25	33.9
$RhCu/SiO_2$	21.1	5.63	0.67	6.30	14.8	29.7
$RhZn/SiO_2$	1.15	0.24	0.57	0.81	0.34	70.4

[a] Including *n*-propanol and minor amount of isopropanol.

[b] Including propanal, *n*-propanol and isopropanol.

CO pulse titration was conducted on the AutoChem II 2920 chemisorption analyzer. 50 mg sample was used for each time and reduced at 450 °C in a 50 mL/min 10% H_2/Ar gas flow for 30 min. After cooling to room temperature in He, pulse of 10% CO/He was repeated till saturated adsorption of CO. The CO uptake amounts of Rh/SiO_2, $RhCo/SiO_2$ and $RhNi/SiO_2$ are listed in Table S4. The increased CO uptake over $RhNi/SiO_2$ compared with Rh/SiO_2 reflects more exposure of Rh atoms on particle surface with dilution by Ni, though these two catalysts have similar average particle sizes of 2.9 nm (Fig. 3), and surface Ni may also adsorb CO. The decreased CO uptake of $RhCo/SiO_2$ is attributed to largely weakened CO adsorption strength with Co alloying (Fig. 7), and Co hardly adsorbs CO at low pressures. This explanation is validated by conducting the CO pulse at 0 °C that results in an increased uptake. TOF in Fig. 6b was calculated according to CO uptake at room temperature of each catalyst.

Table S4. CO uptake of the catalysts in CO pulse titration.

Catalyst	**CO uptake (μmol/g)**
Rh/SiO_2 (room temperature)	28.2
$RhCo/SiO_2$ (room temperature)	15.4
$RhCo/SiO_2$ (0 °C)	24.2
$RhNi/SiO_2$ (room temperature)	47.9