Supporting Information for

High-Pressure NO-Induced Mixed Phase on Rh(111):
Chemically Driven Replacement

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1. Optimized Geometric Parameters

We summarized the calculated geometric parameters for the four structures after optimization, which are discussed in the text.

For the $c(4 \times 2)$-2NO and $p(2 \times 2)$-3NO structures, the obtained values are similar to those of previous reports.[1–3] In the present case, the top-NO molecule has an upright configuration with the molecular axis perpendicular to the surface. We tested several tilted NO configurations as the initial guess. The inclined NO molecule stands up to almost the surface normal after optimization. The tilt angle is converged to ~10˚. The energy difference between the tilted and upright NO is ~0.01 eV.

Table S1. Optimized geometric parameters. d_{A-B} is a bond length from an atom (A) to other one (B), whereas h_{A-B} is a vertical separation. α is a tilt angle of NO molecule form the surface normal. Δz is a buckling displacement of the topmost Rh atom underneath top-NO from the averaged surface level.

System	Sites	d_{Rh-N} (Å)	d_{N-O} (Å)	d_{Rh-O} (Å)	h_{Rh-N} (Å)	h_{Rh-O} (Å)	α (°)	Δz (Å)
$c(4 \times 2)$-2NO	H	2.03/2.07	1.21		1.38	2.59	3.55	
	F	2.03/2.07	1.21		1.39	2.60	3.41	
$p(2 \times 2)$-3NO	H	2.07	1.22		1.35	2.57	0	
	F	2.06	1.22		1.36	2.57	0.01	
	T	1.79	1.17		1.79	2.96	0	0.166
$p(2 \times 2)$-2NO+O	H	2.07	1.21		1.37	2.59	0	
	F			2.03		1.29		
	T	1.79	1.17		1.79	2.96	0	0.135
$p(2 \times 2)$-NO+2O	H			2.02		1.28		
	F			2.02		1.30		
	T	1.79	1.17		1.79	2.96	0	0.123

2. Calculated Adsorption Energies

The average adsorption energy (E_{ad}) was calculated for NO/Rh(111), N/Rh(111) and O/Rh(111) systems. The results are shown in Table S2.

Adsorption energies for possible NO adsorbed structures were estimated using a following procedure;

$$E_{ad} = (E_{NO/Rh(111)} - E_{Rh(111)} - N \times E_{NO})/N, \quad (1)$$

where $E_{NO/Rh(111)}$, $E_{Rh(111)}$, and E_{NO} are the total energies of NO/Rh(111), bare Rh(111), and isolated NO molecule, respectively and N is the number of adsorbed NO molecules per unit cell. We applied a similar way for the case of N and O adsorption.

The NO molecule could be stabilized for all the high-symmetry adsorption sites at 0.25 ML. The hcp-hollow site is the energetically most favorable for NO molecule, whereas the fcc-hollow site is favored for atomic O. The N atom has a relatively week interaction with Rh(111) surface. The N and O atoms were not stabilized at bridge site and displaced to the adjacent hollow site.

The results of average adsorption energy at 0.50 ML revealed the $c(4 \times 2)$-2NO is more stable than the $p(2 \times 2)$-2NO. This is in agreement with our experimental observations. The adsorption energy for the $p(2 \times 2)$-3NO structure is large enough to stabilize this structure.

Table S2. Calculated adsorption energies of NO, N and O on Rh(111). The adsorption energies are estimated with respect to gas-phase free molecule. Several adsorption phases of NO, N and O with different structures are considered

Coverage (ML)	System	NO (eV)	N (eV)	O (eV)
0.25	$p(2 \times 2)$ (H)	−2.41	−0.202	−1.94
	$p(2 \times 2)$ (F)	−2.31	−0.0379	−2.00
	$p(2 \times 2)$ (B)	−2.27	−	−
	$p(2 \times 2)$ (T)	−1.93[a]	−	−0.575
0.50	$c(4 \times 2)$ (HF)	−2.41		
	$p(2 \times 2)$ (HF)	−2.33		
0.75	$p(2 \times 2)$ (HFT)	−2.07[b]		

[a] NO molecule at on-top site has the upright configuration.

3. XPS Observation for O-Covered Surface

N−O bond dissociation and generation of adsorbed atomic species proceed efficiently on the Rh surface above room temperature (RT). We observed an NO and O mixed phase with XP spectra as shown in Fig. 3. To investigate the contribution of adsorbed O, we have measured the O 1s and Rh $3d_{5/2}$ levels for an O-adsorbed phase intentionally formed on the Rh(111) surface..

The O covered surface was prepared by O_2 exposure at 10^{-7} Torr for 10 minutes (i.e. 60 Langmuir) at RT. A single peak is observed at 529.7 eV as shown in Fig. S1(a), which is assigned to the chemisorbed O. It is known that the O atom prefers the fcc-hollow site, which is also supported by our calculations (Table S2). The Rh $3d_{5/2}$ level is deconvoluted into three components. The middle one at 307.3 eV is contribution from the bulk Rh atoms. The other two components at 307.2 and 307.6 eV are assigned to lower-coordinated (1/3) and higher-coordinated (2/3) surface Rh atoms, respectively. Even at the saturated coverage, the $p(2 \times 1)$-1O structure (0.50 ML) has a lower-coordinated Rh in the unit-cell,[4] though the intensity ratio of the two surface Rh species should be unity in case of the perfect p(2 × 1)-1O structure. Köhler et al. reported that a dense O-induced phase is formed at 400 K and under 10^{-3} mbar of O_2.[5] Nevertheless it contains lower-coordinated Rh species in the surface layer.
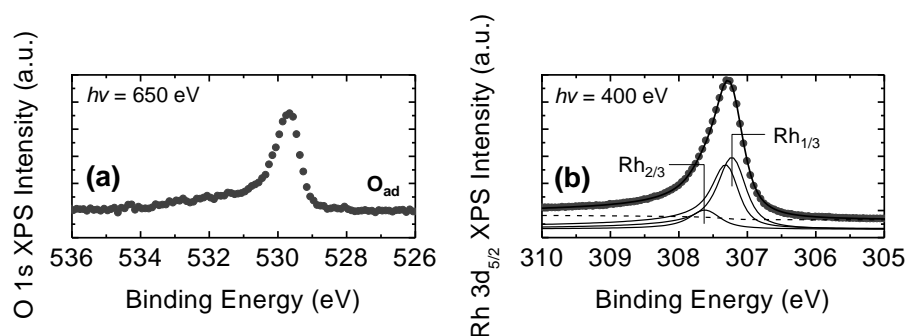
Figure S1. XP spectra from O 1s (a) and Rh $3d_{5/2}$ (b) levels from an O-adsorbed Rh(111) surface at RT. Irradiated photon energies are indicated in each figure.

4. XPS Observation at Room Temperature under Different NO Pressures

XP spectra taken at RT under different pressures are shown in Figure S2(a-c). O 1s spectra (a) show three peaks at 529.5 eV, 530.8 eV and 532.8 eV, which are associate with atomic O, hollow-NO and top-NO, respectively. Even at 10^{-7} Torr, NO molecules partly dissociate into atomic O and atomic N. The partial dissociation is also confirmed by N 1s spectra (b): A broad peak at ~397.5 eV is attributed to atomic N and an asymmetric peak at 400 eV is assigned as NO molecules located at the hollow and top sites. LEED pattern shown in (d) indicates that the adsorbate layer is disordered after NO gas exposure at 10^{-7} Torr. The atomic N is removed by gaseous NO at elevated pressures (1 mTorr and 10 mTorr), while the atomic O remains on the surface even under the elevated pressures. The O 1s and N 1s spectra show that the populations of hollow-NO and top-NO are increased at the elevated pressures. As for the Rh $3d_{5/2}$ spectra exhibit no significant change at different NO pressures. This means that the occupancy of the hollow sites and the top sites of surface Rh layer is almost the same irrespective of NO pressure, though the relative populations among the adsorbates (hollow-NO, atop-NO, atomic O and atomic N) occupying the above sites are changed.
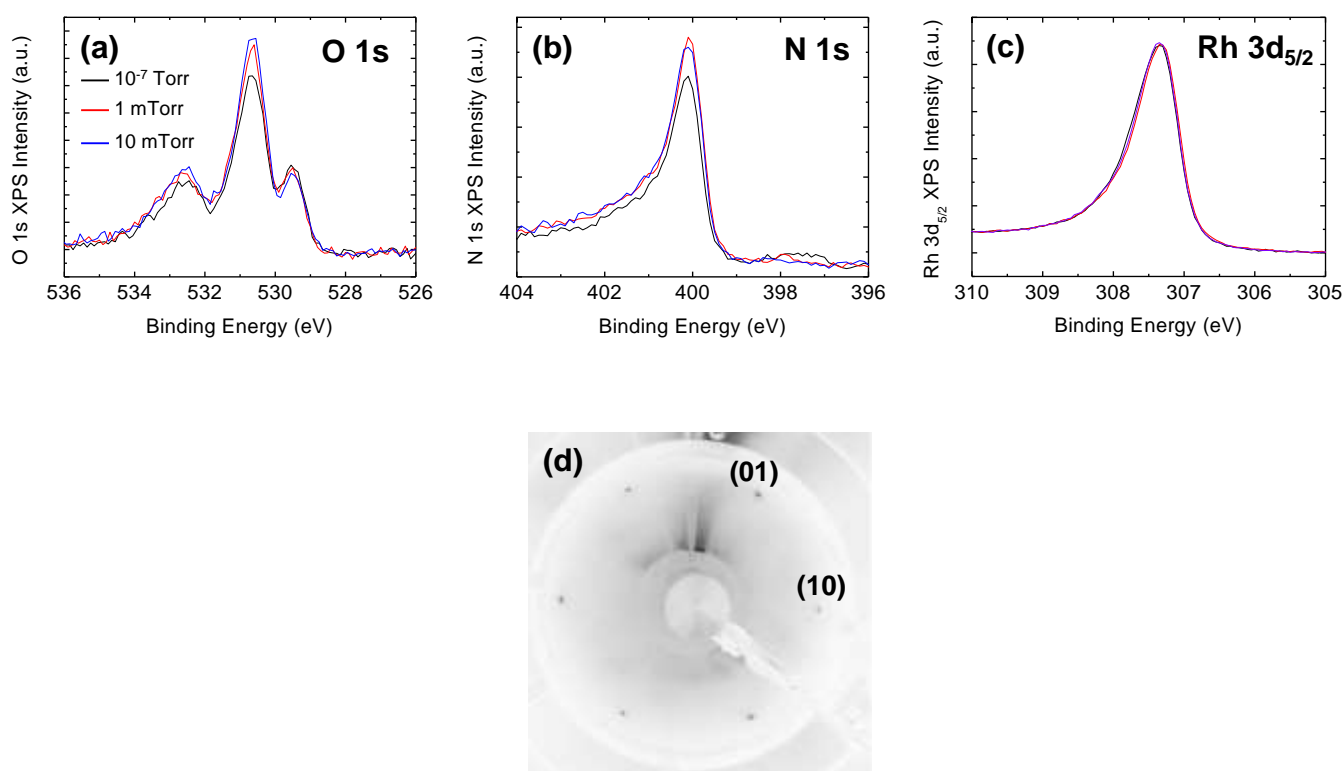
Figure S2. XP spectra in O1s level (a), N 1s level (b) and Rh $3d_{5/2}$ level (c) for a Rh(111) surface taken at RT under exposure of NO with different pressures (10^{-7} Torr (black), 1 mTorr (red) and 10 mTorr (blue)). (d) LEED pattern observed after NO gas exposure at 10^{-7} Torr and subsequent evacuation at RT.

5. References

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