Catalysis on singly dispersed bimetallic sites

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A catalytic site typically consists of one or more atoms of a catalyst surface that arrange into a configuration offering a specific electronic structure for adsorbing or dissociating reactant molecules. The catalytic activity of adjacent bimetallic sites of metallic nanoparticles has been studied previously. An isolated bimetallic site supported on a non-metallic surface could exhibit a distinctly different catalytic performance owing to the cationic state of the singly dispersed bimetallic site and the minimized choices of binding configurations of a reactant molecule compared with continuously packed bimetallic sites. Here we report that isolated Rh1Co3 bimetallic sites exhibit a distinctly different catalytic performance in reduction of nitric oxide with carbon monoxide at low temperature, resulting from strong adsorption of two nitric oxide molecules and a nitrous oxide intermediate on Rh1Co3 sites and following a low-barrier pathway dissociation to dinitrogen and an oxygen atom. This observation suggests a method to develop catalysts with high selectivity.
A single reaction event of heterogeneous catalysis occurs on a specific catalytic site at atomic or nanoscale. An active catalytic site catalyses a reaction by decreasing its activation barrier through a reaction pathway different from that without a catalyst. Typically, a catalytic site may consist of one, two or a few atoms of surface of a catalyst particle. Atoms of a catalytic site arrange into a configuration that essentially offers a specific electronic structure for the catalytic cycle. Bimetallic nanoparticle catalysts play significant roles in chemical and energy transformations since the second metal (A) could tune catalytic performance of a monometallic catalyst (M) through ligand effect, geometric effect, bi-functional effect or lattice strain effect (Fig. 1a,b). Atoms of a catalytic site of a bimetallic nanoparticle could come from more than one element (for example, M and A in Fig. 1c). Alternatively, they could come from the same element (for example, M in Fig. 1d) though surface of the bimetallic nanoparticles has both elements M and A. In the latter case, atoms of element A are the modifier of electronic structure but do not directly participate into the catalysis. When metal atoms of a catalytic site come from two different metal elements such as M and A, we term it a 'bimetallic' site (Fig. 1c); in this case, atoms from both M and A directly participate into the catalytic reaction. One type of such bimetallic sites is referred to M\_A\_n (M and A: metal elements, n ≥ 1), in which both M and A directly participate into a catalytic reaction. The feature of such a bimetallic site is that there is only one atom of M though there is one or more atoms of A.

Typically, such a bimetallic site, M\_A\_n, is continuously packed on surface of a bimetallic nanoparticle. Thus, the M\_A\_n sites on surface of a bimetallic nanoparticle are at a metallic state. However, if such bimetallic sites (M\_A\_n) are separately anchored on the surface of a non-metallic support such as a transition metal oxide, these isolated bimetallic sites (Fig. 1f) are at cationic state. Such isolated bimetallic sites could provide a different surface process including adsorption and dissociation for a reactant molecule or/and an intermediate compared with continuously packed bimetallic sites on a bimetallic nanoparticle. Such a different surface process could facilitate dissociation of a reactant molecule and then accelerate a subsequent coupling with another reactant molecule/dissociated species to form an intermediate or a product molecule. In addition, the single dispersion of atom M of an isolated bimetallic site (M\_A\_n) minimizes choices of potential binding configurations of a reactant molecule, dissociated species, or intermediate on catalyst surface (Fig. 1f), in contrast to the potential multiple choices of binding configurations such as on-top, bridge or hollow sites on the surface of a bimetallic nanoparticle. For example, on an M–A bimetallic nanoparticle surface, a R\_2 molecule could bind to atop, bridge or even hollow site of M atoms. However, R\_2 can bind to M atom through only an atop binding (Fig. 1f) on an isolated bimetallic site M\_A\_n. Consequently, the minimized choices of binding configurations of reactant, dissociated species or intermediate on isolated M\_A\_n sites may enhance catalytic selectivity by following a specific reaction pathway if there are multiple pathways on a bimetallic nanoparticle.

Here we report the preparation of a catalyst consisting of singly dispersed bimetallic sites (SBMS) Rh\_1Co\_3 through controlled oxidation and reduction processes with the aid of in situ track of evolution of chemistry and structure of the catalyst precursor, and the unique catalytic performance of Rh\_1Co\_3 in terms of 100% selectivity for reducing NO to N\_2 at 110°C with a much higher activity than Rh–Co bimetallic nanoparticles at this temperature. Our results illustrate that isolation of bimetallic sites of bimetallic nanoparticles could be used to develop catalysts with higher selectivity or activity.

**Results**

**Synthesis of a catalyst of isolated bimetallic sites Rh\_1Co\_3.** As shown in Fig. 2, the synthesis of a catalyst of isolated bimetallic sites begins with the formation of hydroxide species M(OH)\_2 on the surface of a reducible oxide A\_nO\_y, followed by a calcination at 150°C in O\_2 to anchor M to the surface through formation of M–O–A bonds between singly dispersed M(OH)\_2 species and the surface of the support A\_nO\_y, and concluded with a controlled reduction at 300°C in 5% H\_2 to remove some of the oxygen atoms bonded to both atom M\_1 and atoms A of the surface, thus forming M–A bonds on the surface of the oxide (Fig. 2).

An over-reduction of the support A\_nO\_y typically forms an ultrathin bimetallic film of metals M and A; in this case, the guest metal atoms M may alloy with metal atoms of A to form a bimetallic thin layers (Supplementary Fig. 1) instead of isolated M\_A\_n bimetallic sites. On the other hand, a less reduction in terms of a reduction at a relatively low temperature could not remove oxygen atoms between M\_1 and A of M\_1O\_y/A\_nO\_z; in this case, R\_1 and R\_2 only bind to atoms of metal M instead of A; A is only the modifier of electronic or geometric structure.
In a reducing environment, the guest metal atom M forms singly dispersed bimetallic sites M1A, which are isolated. They are called singly dispersed bimetallic sites.

**Figure 3** In situ studies of surface chemistry. **In situ** studies of surface chemistry of the catalyst precursor in the preparation of the catalysts of singly dispersed Rh1Co3 bimetallic sites with ambient pressure XPS. (a) Rh 3d photoemission features during oxidation and reduction processes as marked. (b) Co 2p photoemission features during oxidation and reduction. (c) Evolution of O/Co atomic ratio under different reaction conditions; the error bar is ±5% of the measured data. (d) HAADF-STEM image (14 × 11 nm) of Rh1Co3/CoO prepared with oxidation at 150 °C in 5% O2 and reduction at 300 °C in 5% H2; the bright spots are Rh atoms of Rh1Co3 catalytic sites; Rh1Co3 sites are singly dispersed.

During oxidation in O2, Rh atoms are at a cationic state with a high binding energy of Rh 3d5/2 at 309.4 eV (Fig. 3a). Upon the formation of Rh1Co3, species on CoOx and reduction of H2, the binding energy of Rh was reduced to 308.5 eV at 300 °C (Fig. 3a). A controlled reduction in 5% H2 resulted in a binding energy of 308.5 eV instead of 307.4 eV of metallic Rh, which suggests a change in the binding environment of Rh atoms during the reduction. The down-shift to 308.5 eV indicates that the Rh atoms of the catalyst upon a reduction at 300 °C in 5% H2 are not at a metallic state. Figure 4d is the image of HAADF-STEM (high-angle annular dark-field) through STEM (scanning transmission electron microscopy) of Rh1Co3/CoO after catalysis at 400 °C, in which singly dispersed Rh atoms appear as separated spots with high contrast due to the larger atomic number of Rh atoms in contrast to Co (ref. 13). This is consistent with the single dispersion of Rh atoms of catalysts after catalysis at 400 °C confirmed with in situ EXAFS (Fig. 4a).

**Figure 2** Schematic of synthesis of a catalyst of singly dispersed bimetallic sites M1A. (a) Well-crystallized reducible oxide substrate, A2Ox. (b) Deposition of hydroxide species of guest metal, M(OH)x, on the surface of the oxide support, A2Ox; a low concentration of M cations allows them to be singly dispersed on the surface of A2Ox, the atomic ratio of M atoms to A atoms at the topmost layer of atoms A of A2Ox is typically <5-10% of M(OH)x, species are weakly bound to the surface of A2Ox. (c) Formation of singly dispersed M1Ox species upon oxidation in 5% O2 at 150 °C; M cations are bonded to A2Ox surface through M-O-A bonds. (d) A controlled reduction in 5% H2; removal of oxygen atoms between M and A atoms by reduction in H2 makes M directly bond with A atoms of oxide support, forming an M1A site; as M atoms are singly dispersed on A2Ox (due to the low concentration of guest atoms M), the formed M1A, bimetallic sites are isolated. They are called singly dispersed bimetallic sites.
Figure 4 | Characterizations in the preparation of isolated bimetallic sites. Characterizations in the preparation of isolated bimetallic sites Rh1Co3/CoO and during catalysis by in situ EXAFS, in situ AP-XPS, and ex situ HAADF-STEM. (a) r-Space spectra of Rh K edge of catalyst precursor at 150 °C in O2 (black line), a following reduction at 300 °C in H2 (red line) and during catalysis at 400 °C from in situ EXAFS studies (blue line). (b) Photoemission feature of Rh 3d of catalyst precursor at 150 °C in O2 (black line), a following reduction at 300 °C in H2 (red line) and during catalysis at 400 °C (blue line) from in situ AP-XPS studies. (c) TEM image (700 × 700 nm) of Rh1Co3/CoO after catalysis. (d) HAADF-STEM image of the catalyst of isolated Rh1Co3 bimetallic sites after catalysis at 400 °C; the red arrows mark the Rh atoms that are singly dispersed on CoO.

Table 1 | Coordination numbers and bond lengths.

| Reaction temperature | Reactants | Measurement condition | N(Rh–O) | N(Rh–Co) | N(Rh–Rh) | R(Rh–O) (Å) | R(Rh–Co) (Å) |
|----------------------|-----------|-----------------------|---------|----------|----------|-------------|--------------|
| 150 °C               | O2        | 25°C, O2              | 4.5 ± 0.6 | 0.3 ± 0.4 | 0        | 2.033 ± 0.008 | 2.55 ± 0.03  |
| 300 °C               | H2        | 25°C, CO + NO         | 2.6 ± 1.0 | 1.8 ± 0.9 | 0        | 2.13 ± 0.04  | 2.61 ± 0.02  |
| 400 °C               | CO + NO  | 25°C, CO + NO         | 1.7 ± 0.5 | 1.3 ± 0.7 | 0        | 2.15 ± 0.03  | 2.60 ± 0.02  |

Coordination number of O, Co and Rh atoms around a Rh atom and bond lengths of Rh–O and Rh–Co based on EXAFS studies of precursor of Rh1Co3/CoO catalyst at 150 °C in 5% O2, 300 °C in 5% H2 and of catalyst of Rh1Co3/CoO during catalysis at 400 °C in a mixture of 5% CO + 5% NO. Still preserves a single dispersion [CN(Rh–Rh) = 0] and bond with cobalt and oxygen atoms, [CN(Co–Rh) = 2.6 and CN(O–Rh) = 1.8]. The direct bonding of Rh to Co (Table 1) shows the formation of Rh–Co bonds. Since a Rh atom is isolated from other Rh atoms and bonds with Co atoms, we term the ensemble Rh1Co3 a singly dispersed bimetallic site or an isolated bimetallic site (Fig. 2d). The average coordination number of Co atoms directly bonded to a Rh atom is almost 2 based on EXAFS studies. For simplicity and consistence with the Rh1Co3 structure on CoO proposed through optimization in the following computational studies, Rh1Co3/CoO is used as the term of this type of isolated bimetallic sites in this communication.

It is noted that an over-reduction in 5% H2 at a relatively high temperature of 400 °C forms metallic Co surface layers consisting of a small amount of Rh atoms, as is evidenced by the low binding energy of Co 2p3/2 at 778.3 eV and Rh 3d5/2 at 307.2 eV (Supplementary Fig. 1). However, AP-XPS studies show that a reduction in 5% H2 at 250 °C does not form a Rh–Co bond since Rh 3d5/2 is still ~309.0 eV instead of 308.5 eV (Fig. 3). Thus, an appropriate reduction temperature is the key for the formation of Rh1Co3 bimetallic sites.

Other than the evolution of coordination environment of Rh atoms in the preparation of a catalyst, one obvious change of the support, CoO, during reduction at 300 °C in 5% H2 is the formation of cobalt monoxide in the surface region, evidenced by the observed new peak of Co 2p3/2 at 786.4 eV (Fig. 3b). This peak is attributed to the characteristic satellite peak of Co 2p3/2 of Co2+ in an octahedral coordination with oxygen atoms in CoO at 786.4 eV (refs 14,15). Thus, by referring to the characteristic satellite peak of Co 2p3/2 of CoO reported in literature14,15, the photoemission feature of Co 2p3/2 collected at 300 °C in 5% H2 is assigned to CoO. In addition, the formation of CoO is also supported by the O/C atomic ratio of the catalyst experiencing a reduction at 300 °C in 5% H2, 0.80 (Fig. 3c), which was measured by taking the stoichiometric ratio of Co3O4, 1.33 at room temperature as a reference to calibrate the measured atomic ratios (O/Co).

As shown in Supplementary Table 1, the theoretical atomic ratio of all Rh atoms to all Co atoms of the topmost layer of CoO nanoparticles is 1.40%. The measured ratios of the catalyst during catalysis at 150 °C and 400 °C are 1.26 and 1.25%, respectively (Supplementary Table 1), which are quite close to the calculated ideal value, 1.40% (Supplementary Methods). These studies suggest that Rh atoms are mainly located on the topmost surface of catalyst particles without obvious thermal diffusion to deep layers. More information on the calculation of these atomic ratios of Rh to Co can be found in Supplementary Methods and Supplementary Figs 11–14.

Catalytic performances of isolated and continuous bimetallic sites. After the oxidation of the catalyst precursor in 5% O2 at 150 °C with a following reduction at 300 °C in 5% H2, the catalyst was cooled to 80 °C in 5% H2. Once the 5% H2 was purged, 30 ml min−1 10% CO (balanced with Ar), 20 ml min−1 5% NO (balanced with Ar) and 10 ml min−1 99.999% Ar were mixed and then introduced. Measurements of catalytic performance on the catalyst of isolated Rh1Co3 sites anchored on CoO, Rh1Co3/CoO were performed in a fixed-bed flow reactor. N2O is the by-product of this reaction. Rh1Co3/CoO exhibits a catalytic selectivity of 100% for the production of N2 at a temperature as low as 110 °C (Fig. 5a).
on SiO2 is not active at any temperatures < 250 °C (Fig. 5b). In addition, the activity and selectivity for the production of N2 on Rh–Co bimetallic nanoparticles supported on CoO at 110 °C are only 20% and 10%, respectively (Fig. 5d). Compared with Rh–Co bimetallic nanoparticles supported on CoO, obviously the isolated bimetallic sites Rh1Co3 supported on CoO exhibit an outstanding
catalytic performance in terms of high catalytic activity and 100% selectivity for production of N₂ at a temperature as low as 110 °C (Fig. 5a). Supplementary Table 2 lists catalytic performances at 110 °C measured under kinetics controlled regime (Fig. 5e-g). Clearly, isolated Rh₁Co₃ bimetallic sites anchored on CoO (Rh₁Co₃/CoO) exhibit a much higher activity than Rh–Co bimetallic nanoparticles supported on SiO₂, pure CoO and Rh–Co bimetallic nanoparticles supported on CoO. It is noted that Rh nanoparticles16 or Rh-based bimetallic nanoparticles17–20 and Rh single crystals21 are not active at a temperature <240 °C; selectivities for the production of N₂ on Rh nanoparticles at 240 °C (ref. 16) and Rh(100) at 255 °C (ref. 21) are only ~30% and ~25%, respectively. Overall, the isolated bimetallic sites Rh₁Co₃ of Rh₁Co₃/CoO exhibit an outstanding catalytic performance in terms of quite high catalytic activity and 100% selectivity for the reduction of NO to N₂ at a temperature as low as 110 °C.

In situ AP-XPS studies of the catalyst during catalysis at a temperature up to 400 °C showed that Rh atoms of Rh₁Co₃/CoO catalyst remains at its oxidizing state (Fig. 4b). The high binding energy of Rh 3d of isolated Rh₁Co₃ sites anchored on CoO, 308.5 eV, suggests the cationic nature of the Rh atoms in isolated bimetallic sites during catalysis at 400 °C. The preservation of single dispersion of the Rh atoms and the coordination of Co to Rh were supported by in situ studies of EXAFS during catalysis (Fig. 4a and Table 1) and ex situ studies of the catalyst after catalysis at 400 °C using HAADF-STEM (Fig. 4d). These characterizations suggest that the isolated bimetallic sites are preserved during catalysis and responsible for the high activity and 100% selectivity for N₂ production. In addition, catalytic performances of Rh₁Co₃/CoO and pure CoO under kinetics-controlled regions were measured (Fig. 5e-g). By using the number of Rh atoms as the number of Rh₁Co₃ sites, turnover frequencies (TOFs) of the production of N₂ were calculated and listed in Supplementary Table 2. The turnover frequency of Rh₁Co₃/CoO at 110 °C is 4.4 N₂ molecules per bimetallic site per second.

To confirm the importance of direct bonding of Co atoms to a Rh atom in Rh₁Co₃/CoO, catalyst Rh₁Oₓ/CoO was synthesized with the method described in the Methods section. A two-step method was used in the preparation of Rh₁Oₓ/CoO. CoO substrate was prepared by annealing Co₃O₄ to 300 °C in 5% H₂; the phase transformation was confirmed with XRD; in the second step Rh cations are loaded to the surface of CoO through deposition–precipitation with a following calcination in H₂ at 200 °C for 1 h; the adsorbed Rh(OH)₂ species were transferred to Rh₁Oₓ. The existence of Rh atoms on the surface was supported with the preservation of Rh/Co ratio (all Rh atoms to all Co atoms of the topmost layer of Co of CoO) measured with AP-XPS before and after annealing in H₂ at 200 °C.

The difference in coordination environment of Rh₁ between Rh₁Co₃/CoO and Rh₁Oₓ/CoO results in a distinct difference in catalytic performance. Figure 5e,f present the catalytic performances of Rh₁Co₃/CoO and Rh₁Oₓ/CoO measured under kinetics-control regime. Rh₁Oₓ/CoO is not active at a temperature of 150 °C and lower. But Rh₁Co₃/CoO is active at 110 °C. In addition, Rh₁Oₓ/CoO exhibits low selectivity to N₂ production in the temperature range of 150–200 °C. But Rh₁Co₃/CoO exhibits a selectivity of 100% for the reduction of NO to N₂ in this temperature range. The distinct difference between Rh₁Oₓ/CoO and Rh₁Co₃/CoO in their catalytic performances results from two factors. One is the difference in geometry; the Rh–O–Co of Rh₁Oₓ/CoO is different from a bimetallic site of Rh₁Co₃/CoO. The existence of a Co–Rh₁–Co on Rh₁Co₃/CoO allows for a strong bonding of two NO molecules (see the following DFT calculations) and thus readily activate NO molecules compared with Rh₁Oₓ/CoO. Thus, catalyst of singly dispersed bimetallic sites Rh₁Co₃ is different from the singly dispersed Rh₁ atoms that solely bond to oxygen atoms of the oxide support22–24.

Location of Rh atoms on CoO. To understand the catalytic mechanism of NO reduction with CO on singly dispersed Rh₁Co₃ anchored on cobalt monoxide, computational modelling of the adsorption, activation and reaction pathway using periodic density functional theory (DFT) was performed. DFT calculations were done for interpretation of the binding environment of Rh atoms (Fig. 6). A Rh atom could anchor to the original position of a missed oxygen (the location of an oxygen vacancy) of CoO in Fig. 6a and thus bond to cobalt atoms; alternatively, it could replace a Co atom of CoO therefore bond to oxygen atoms (Fig. 6c). As shown in Fig. 6a, DFT calculations show that the energy change for filling an oxygen vacancy with a Rh atom is −5.39 eV, while the energy change for the replacement of a Co atom with a Rh atom on surface is −3.86 eV. Obviously, filling an oxygen vacancy of CoO with a guest Rh atom is energetically favourable than replacing a Co atom of the surface with a guest Rh atom. This is consistent with the in situ measurements of EXAFS of the catalyst at 5% H₂ at 300 °C showing that Rh atoms bond with Co atoms (Fig. 4a and Table 1). Supplementary Fig. 5b is the optimized structure in which the guest Rh atom fills an oxygen vacancy and thus bonds with three cobalt atoms and one oxygen atom.

Optimization of Rh₁Co₃ structural model. In rock-salt CoO crystal, each Co²⁺ is coordinated by six O²⁻ ions in an octahedral crystal field with Co–O distance of 2.13 Å. The (011) surface of CoO with oxygen vacancies can be viewed as an assembled –O–Co–O–Co–O–Co– chain (Supplementary Fig. 5a). When a Rh atom substitutes an oxygen atom on the CoO surface, the Rh₁ atom is not only relocated by 1.13 Å above the surface Rh and Co atoms can adsorb NO and CO, the previous calculations found that adsorption of one NO molecule (Supplementary Fig. 5b) in the neighbouring chain with a Rh₁–O distance of 2.04 Å, which is close to a Co–O single bond estimated as 1.9 Å. As a result, the Rh₁ atom only bonds with one neighbouring O atom, while other O atoms are far from the Rh₁ atom by more than 3.3 Å away. In addition, around a Rh₁ atom, there are three Co atoms Co(3), Co(5), Co(7) marked with stars with a Rh–Co distance averagely 2.54 Å in Supplementary Fig. 5b. However, other three cobalt atoms, Co(2), Co(4) and Co(6) around the Rh₁ atom are far from the Rh₁ at a distance of Rh₁–Co(2) at 3.15 Å, Rh₁–Co(4) at 2.81 Å and Rh₁–Co(6) at 3.15 Å. Therefore, the local coordination shell of Rh₁ atom is referred as Rh₁Co₃; the three Co atoms directly coordinating to Rh₁ of Rh₁Co₃ are Co(3), Co(5) and Co(7). This optimized geometry model will be used in all the following calculations.

Adsorption geometry of NO and CO on Rh₁Co₃/CoO. As both the surface Rh and Co atoms can adsorb NO and CO, the preferred adsorption models of NO and CO (Supplementary Fig. 5c–j) were investigated through DFT calculations. Consistent with the orbital interaction analysis, the NO and CO interact with metal atoms through N- and C-side, respectively. By optimizing the adsorption geometries of NO and CO on various sites with different end-on and bridging binding configurations, the adsorption modes and energies of CO and NO on the surface of a Rh₁Co₃/CoO catalyst were evaluated in the DFT calculations. It is found that adsorption of one NO molecule (Supplementary Fig. 5c) on Rh₁ atom is slightly more favourable than that of one
CO molecule (Supplementary Fig. 5d). Because the singly dispersed Rh atom is not saturated in its coordination shell, co-adsorption is in fact more stable than mono-adsorption. Among all the possible co-adsorption models (Supplementary Fig. 5e–j), two NO molecules co-adsorbed on the Co–Rh₁–Co of Rh₁Co₃ is most stable (Supplementary Fig. 5e). Thus, Rh₁Co₃ adsorbing two NO molecules was used to simulate the reaction pathways and search transition states in the following catalysis studies. Similar to the results for Rh₁Co₃/CoO(011), DFT calculations of the adsorption energies of NO, NO⁺, CO⁺ or CO⁺ + NO on Rh₁Co₃/CoO(001) (Supplementary Fig. 6) show that co-adsorption of two NO molecules on Co–Rh₁–Co of Rh₁Co₃/CoO are the strongest adsorption as well.

**Reaction pathway.** The reaction pathway was calculated for the reduction of NO with CO on a singly dispersed Rh₁Co₃ bimetallic site anchored on CoO (Fig. 7). Briefly, the Ovac is filled by a single Rh atom to form a singly dispersed bimetallic site Rh₁Co₃ (step i), which can adsorb two NO molecules on the Co–Rh₁–Co atoms of Rh₁Co₃ (step ii), thus forming a Rh₁Co₃ bimetallic site. Two NO molecules can adsorb on Rh₁Co₃/CoO(001) (Supplementary Fig. 6) and the adsorption energy is calculated. The reaction pathway is calculated for the reduction of NO with CO on the singly dispersed Rh₁Co₃ supported on CoO proposed from DFT calculations. (a) Reaction pathway and energy profile. (b) Calculated structural parameters of intermediates and transition states in the pathway.
a Rh1Co3 site (step ii); two NO molecules couple on Co–Rh1–Co to form a N2O2 intermediate (step iii) to facilitate the formation of intermediate N2O; meanwhile one CO molecule can adsorb on the Co atom neighbouring to Rh1Co3 (step iv).

The first CO2 molecule is released after the adsorbed CO molecule couples with one O atom of N2O3 adsorbed on the Co–Rh1–Co site (TS-1). This coupling yields a CO2 molecule and forms an intermediate N2O remaining on the surface (step v). It is noted that the N–O bond in the intermediate N2O stretches to form a transition state with a small barrier of 0.21 eV (TS-2), which leads to a ready cleavage of N–O bond of the intermediate N2O and then releases a N2 molecule and leaves an O atom on Rh1 (step vi). By adsorbing a second CO on a nearby Co atom (step vii) and then coupling to the left oxygen atoms on the Rh1 atom, a second CO2 molecule is released from the surface; thus a catalytic cycle is finished. In this catalytic cycle, the catalyst releases two CO2 molecules and one N2 molecule and then recovers its original surface structure (step i in Fig. 7). The inset of Fig. 7a presents the calculated energy profile with the partially reduced system as the reference for the energies in eV. Figure 7b lists the calculated structural parameters of intermediates and transition states of this pathway.

In this reaction pathway, the Rh1Co3 site plays a crucial role in the high activity and selectivity in reducing NO with CO. The local coordination environment of the bimetallic site Rh1Co3 helps to activate the two NO molecules on Co–Rh1–Co of Rh1Co3 through co-adsorption and coupling. The catalytic elementary steps, evolution of energies and activation barriers are listed in Table 2. Especially noteworthy is the extremely low activation barrier of N2O decomposition (0.21 eV) to a N2 molecule on the Rh1Co3/CoO catalyst. Given the high reaction temperature, this step is virtually barrierless in terms of Gibbs free energies. Thus, these calculation results are quite consistent with the fact that the Rh1Co3 bimetallic sites are active at a temperature as low as 110°C with a selectivity of 100% for production of N2.

The computed electron density difference maps of the two different fragments on Rh1Co3/CoO and Rh–Co bimetallic nanoparticle/CoO are shown in Supplementary Fig. 8c and d, respectively. In these plots (Supplementary Fig. 8c and d), a decrease in electron density is shown in blue, electron enrichment is indicated in red; white region indicates little change in electron density. The more red colour between N and Rh in Rh1Co3/CoO (Supplementary Fig. 8c) than the one in the Rh–Co bimetallic nanoparticle/CoO. The calculated Bader charges (Supplementary Table 4) revealed that the Rh1 single atom of Rh1Co3/CoO carries positive charge upon adsorption of NO while the Rh atom in Rh–Co alloy nanoparticle/CoO carries negative charge upon NO adsorption. The positive charge on Rh1 of a singly dispersed Rh1Co3 site allows more electron transfer from NO, which enhances the Rh–N bond and thus largely weakens the N–O bond of NO molecule on Rh1Co3.

The spin-polarized projected density of states (PDOS) of the 4d states of Rh atom and the N-2p and O-2p orbitals of adsorbed NO on Rh1Co3/CoO and Rh–Co bimetallic nanoparticle/CoO are shown in Supplementary Fig. 8e and f, respectively. The spin-polarized projected density of states show that below the Fermi level (EF) Rh 4d states in Rh1Co3/CoO catalyst are more localized than the Rh 4d states in Rh–Co bimetallic nanoparticle/CoO. In addition, Rh 4d states in Rh1Co3/CoO (Supplementary Fig. 8e) are mixed better with N 2p and O 2p states than Rh 4d states in Rh–Co bimetallic nanoparticle/CoO (Supplementary Fig. 8f), indicating a strong interaction between Rh1 atom of Rh1Co3 and the adsorbed NO molecule.

One critical difference between a singly dispersed Rh1Co3 site anchored on CoO and a Rh–Co bimetallic nanoparticle supported on CoO is the 100% selectivity for production of N2 in reduction of NO with CO on Rh1Co3 (Fig. 5a). On Rh–Co bimetallic nanoparticle supported on CoO (Fig. 5d), however, selectivity for production of N2 is only 10%. To understand this difference in catalytic selectivity for production of N2O on the two surfaces, structural models of Rh1Co3/CoO and Rh–Co bimetallic nanoparticle/CoO (Supplementary Fig. 9) were built. The calculated adsorption energies of N2O for Rh1Co3/CoO and Rh–Co bimetallic nanoparticles/CoO are ~1.56 and ~0.85 eV, respectively. N2O is the by-product of the reduction of NO with CO; it is also the intermediate for production of N2 (step 5 in Table 2). A stronger binding of N2O prevents it from molecular desorption. Thus, the selectivity for the production of N2O on Rh1Co3/CoO is low since the adsorption of N2O on Rh1Co3/CoO is stronger than that on Rh–Co bimetallic nanoparticle/CoO. In addition, as the activation barrier for dissociating N2O to N2 and

### Table 2 | Process energies and activation barriers.

| Reaction pathway | ΔE (eV) | Ea(eV) |
|------------------|--------|-------|
| 1) 2NO → 2NO*    | −5.39  | −      |
| 2) 2NO → N2O2*   | −4.93  | −      |
| 3) CO → CO*      | −0.71  | −      |
| 4) N2O2* + CO* → N2O + CO2 | − | 1.39 |
| 5) N2O* → N2 + O* | −1.70 | 0.21  |
| 6) CO → CO*      | −1.07  | −      |
| 7) CO* + O2* → CO2* | 0.38 | 1.01  |

Calculated process energies (ΔE) and activation barriers (Ea) for these elementary steps in the reduction of NO and CO on Rh1Co3/CoO in the pathway of Fig. 7. Note: (1) The process energy ΔE is defined as the energy difference between the final state and the initial state. (2) Activation barrier Ea is defined as the difference between the energy of the transition state and the energy of its corresponding initial state.
O on RhCO,CoO is only 0.21 eV (TS-2 in Fig. 7), N2O can readily dissociate to N2 on Rh,CoO at a relatively low temperature. Overall, the stronger binding of N2O on Rh,CoO site and the rather low activation barrier for dissociation of the intermediate N2O to N2 on Rh,CoO, make the reduction of NO to N2 with a high selectivity at a relatively low temperature in contrast to Rh–Co bimetallic nanoparticles/CoO.

As described in literature25, the test temperature of engine of a gasoline vehicle is 1,100 °F (593 °C), stability tests by measurements of conversion and selectivity of the catalyst, Rh,CoO/CoO were performed. Concerning the real hydrothermal conditions in a three-way catalytic reactor, water vapour was also introduced to the reactor to simulate the exhaust of gasoline engines. As shown in literature26, typically the composition of water vapour is 20 times of nitric oxide and carbon monoxide. Thus, stability of 10 mg catalyst was tested in a mixture of 12 ml min−1 NO, 12 ml min−1 CO, 68 ml min−1 Ar and H2O vapour generated from 0.18 ml min−1 water and then introduced to a fixed-bed flow reactor. The molar ratio of NO:CO:H2O is 1:2:20. The conversion and selectivity of this catalyst remained nearly constant within 168 h.

These studies suggest that the isolation of bimetallic sites on non-metallic supports is a promising approach for developing catalysts, since such centres exhibit cationic states and offer the fewest binding configurations for reactant molecules—distinctly different from bimetallic nanoparticles.

**Methods**

**Preparation of isolated Rh,CoO,CoO sites on cobalt oxide.** Co3O4 nanorods were synthesized with a modified wet chemistry method in literature27. To synthesize a catalyst of singly dispersed Rh,CoO on Co3O4, Co3O4 nanorods were synthesized with a modified wet chemistry method and a following calcination at high temperature27,28. Then, species of rhodium precursor were introduced on the crystallized Co3O4 nanorods through a deposition–precipitation with a mass ratio of Rh to Co3O4 of 0.25 wt%.

Rh(NO3)3(Sigma-Aldrich, > 36% Rh basis; 0.28 g) was dissolved in water via a 50 ml volumetric flask. Co3O4 nanorods (0.80 g) was dispersed in 50.0 g deionized water with strong agitation to make a homogeneous black suspension. The pH was then gradually adjusted to 9.0 by ammonium hydroxide solution monitored with a pH meter. After that, the solution was stirred vigorously for another 12 h to reach an equilibrium for a thorough, homogeneous adsorption of Rh3+ ions and followed by washing with deionized water and drying under vacuum. The 70% Rh,CoO precursor was dried in vacuum at 70 °C for at least 12 h. Then it was oxidized and reduced at an appropriate temperature so that the singly dispersed bimetallic sites Rh,CoO can be prepared.

Synthesis of Rh–Co bimetallic nanoparticles supported on CoO and Rh–Co alloy nanoparticles/SiO2 (Rh: 5% wt%) was achieved by aqueous impregnation of Rh and Co precursors to SiO2, NPs or Co3O4 nanorods. Rh(NO3)3·3H2O (Sigma-Aldrich, > 36% Rh basis) and Co(NO3)2·6H2O (Sigma-Aldrich, > 98% pure) were used as precursors of Rh and Co, respectively. The total weight percent of Rh and Co is 5 wt% while keeping the atomic ratios of the loaded Rh and Co identical. Rh(NO3)3·3H2O and Co(NO3)2·6H2O were dissolved in deionized water to make a clear solution. Co3O4 nanorods (0.28 g) were immersed in the solution. The water was gradually evaporated at 60 °C with vigorous stirring and the catalyst was then dried in vacuum at 60 °C for 12 h, followed by calcination in 5% O2 at 150 °C for 3 h. Before catalytic measurement, the catalyst was pretreated at 300 °C in 5% H2.

Rh,CoO was synthesized by introduction of Rh cations to well-prepared CoO by deposition–precipitation with a following annealing in N2 and then a reduction at 200 °C in 5% H2 for 1 h.

**In situ studies using ambient pressure X-ray photoelectron spectroscopy.** In situ studies of surface chemistry of these catalysts were performed on the ambient pressure XPS using monochromated Al Kα in the TaO group11,29,30. The binding energy of catalyst samples were calibrated to Au 4f7/2 at 84.0 eV and Ag 3d5/2 at 368.3 eV (ref. 11). In the AP-XPS studies, one or more reactant gases were introduced into a reactor. A sample is inserted and placed at the cross point of a Rowland circle of the monochromator and trajectory line of photoelectrons in lens of differentially pumped energy analyser. A distance between sample surface and the aperture of pre-lens of the differential pumping stage remains at ~0.5 mm, which is shorter than the mean free paths of photoelectrons travelling in a gaseous environment of 5 Torr.

**Measurements of catalytic performance for reduction of NO with CO.** Reduction of NO with CO on catalysts is performed in a fixed-bed flow reactor. Gas compositions and flow rates were marked in captions of figures. Details of catalytic measurement using our fixed-bed flow reactor can be found in our previous publications9,10.

**In situ studies using XANES and EXAFS.** In situ X-ray absorption spectroscopy (XANES) measurements were performed at the beamline X18B at the National Synchrotron Light Source, Brookhaven National Laboratory. The samples were made by pressing the powders into circular pellets using hydraulic press and transferred onto a sample holder of a Nashner–Adler in situ cell31.

The data in the XANES region of the absorption coefficient were analysed by applying the same procedure for pre-edge line fitting, post-edge curve fitting and edge-step normalization to all the data. The XANES and extended X-ray absorption fine structure (EXAFS) data processing and analysis were performed using the IFEFFIT package32. The EXAFS data modelling and analysis were performed using standard procedures,23–36

**Computational methods.** The calculations were performed with the Vienna Ab initio Simulation Package (VASP version 5.2). Both (001) and (001) surfaces of cobalt monoxide were represented by a periodic slab model constructed using bulk cell dimensions: a = b = c = 4.2667 Å (ref. 37). Only calculation results of (001) surface were described in the main text. Since CoO is antiferromagnetic and has atomic moment on cobalt atoms, the primitive cubic unit cell of CoO was used to build the surface slab, which was previously proved to be the most energetically stable configuration for CoO38. The repeated slabs were separated from their neighbouring images by a 12 Å-width vacuum in the direction perpendicular to the surface. Considering the usually very large relaxations of the CoO surfaces, a slab containing five layers of 60 atoms was chosen. The three top-layer slabs of the surface were allowed to relax while the other layers beneath the surface were frozen during the geometry optimization (Supplementary Fig. 10).

The core and valence electrons were represented by the projector-augmented wave method and plane-wave basis functions with a kinetic energy cut-off of 400 eV. Inasmuch as Rh has non-negligible relativistic effects, the mass–velocity and Darwin relativistic effects were included through the projector-augmented wave potentials. The generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange-correlation functional was used in the calculations. A Monkhorst–Pack grid of size of 2 × 2 × 1 was used to sample the surface Brillouin zone. Ground-state atomic geometries were obtained by minimizing the forces on the atoms to <0.002 eV Å−1. Because of the strong d–electron correlation effects for Co, the calculations were carried out with the DFT + U method. The parameters were set at U = 4 eV and J = 1 eV according to previous reports39,40 and our investigation (Supplementary Tables 5, 6). The transition states were obtained by relaxing the force <0.002 eV Å−1 by using the dimer method40.

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Author contributions

F.T. launched the project of catalysis on singly dispersed bimetallic sites of his NSF Career Award, designed the synthesis, catalysis and in situ characterizations of singly dispersed bimetallic sites, analysed the experimental results and wrote this paper. J.L. designed the theoretical studies and wrote the computational part. S.Z. performed majority of the experiments. L.N. interpretation of the experimental results and participated in the writing. J.-X.L. performed the theoretical calculations. J.L. (Liu) performed HAAADF-STEM. S.Z and A.P. performed the EXAFS experiments. A.I.F. analysed the EXAFS data. J.S. and W.H. collected some of the AP-XP data.

Additional information

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