A nine-atom rhodium–aluminum oxide cluster oxidizes five carbon monoxide molecules

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Noble metals can promote the direct participation of lattice oxygen of very stable oxide materials such as aluminum oxide, to oxidize reactant molecules, while the fundamental mechanism of noble metal catalysis is elusive. Here we report that a single atom of rhodium, a powerful noble metal catalyst, can promote the transfer of five oxygen atoms to oxidize carbon monoxide from a nine-atom rhodium–aluminum oxide cluster. This is a sharp improvement in the field of cluster science where the transfer of at most two oxygen atoms from a doped cluster is more commonly observed. Rhodium functions not only as the preferred trapping site to anchor and oxidize carbon monoxide by the oxygen atoms in direct connection with rhodium but also the primarily oxidative centre to accumulate the large amounts of electrons and the polarity of rhodium is ultimately transformed from positive to negative.
Oxide-supported rhodium (Rh) exhibits extraordinary catalytic activity in a large number of reactions\textsuperscript{1–9} such as the oxidation of carbon monoxide (CO)\textsuperscript{1–3,7}, carbon dioxide methanation\textsuperscript{8}, partial oxidation of methane to syngas\textsuperscript{4,5,9} and so on. It has been reported that trace amounts of Rh can promote direct participation of lattice oxygen of chemically very inert supports such as aluminum oxide (Al\textsubscript{2}O\textsubscript{3}), to oxidize reactant molecules\textsuperscript{1,2,4,5,9}, while the fundamental mechanism is elusive. Exploring the function of Rh in invoking oxygen atoms to oxidize CO (refs 22–26). Here we report that a single Rh atom can unexpectedly promote the transfer of five oxygen atoms to oxidize CO from a nine-atom cluster Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2--15}. In contrast, reported homonuclear aluminum oxide clusters (Al\textsubscript{2}O\textsubscript{3})\textsuperscript{2,22,27} can deliver only one oxygen atom to CO and these reactive clusters such as Al\textsubscript{2}O\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} are all oxygen-rich species. Identification of multiple OAT from a single Rh-atom-doped cluster to reactant molecules is an important step to understand the participation of lattice oxygen promoted by noble metals. This gas-phase study that a nine-atom rhodium–aluminum oxide cluster oxidizes five CO molecules is a sharp improvement in the field of cluster science and provides a strictly molecular level understanding of the fundamental mechanism of noble metal catalysis in the related condensed phase.

**Results**

**Reactivity of rhodium–aluminum oxide clusters with CO.** The Rh\textsubscript{Al}O\textsubscript{m} (m = 2–6) cluster ions were generated by laser ablation of a mixed-metal disk compressed with Rh and Al powders. The generated Rh\textsubscript{Al}O\textsubscript{m} cluster ions were mass-selected, cooled and then interacted with N\textsubscript{2} and CO in an ion trap reactor, as shown in Figs 1 and 2. On the interaction of Rh\textsubscript{Al}O\textsubscript{2} with 150 mPa N\textsubscript{2} (Fig. 1a), weak N\textsubscript{2} adsorption (Rh\textsubscript{Al}O\textsubscript{2}N\textsubscript{2}) and N\textsubscript{2}/O\textsubscript{2} exchange (Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2}N\textsubscript{2}) products were generated. Generation of Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2} suggests the possible presence of superoxide (O\textsubscript{2}--?) or peroxide (O\textsubscript{2}O--) unit in Rh\textsubscript{Al}O\textsubscript{2} (Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2} + N\textsubscript{2} → Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2}N\textsubscript{2} + O\textsubscript{2}). In sharp contrast, on the interaction of Rh\textsubscript{Al}O\textsubscript{2} with CO (Fig. 1b–d), a series of products, from Rh\textsubscript{Al}O\textsubscript{2} to Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2}, were generated gradually with the increase of CO partial pressure from 2 to 13 mPa. Signals Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2} did not appear on the interaction of Rh\textsubscript{Al}O\textsubscript{2} with even high pressure N\textsubscript{2} (Fig. 1a). Additional experimental techniques such as multiphoton ionization\textsuperscript{28,29} employing pulsed lasers are required to observe the neutral CO\textsubscript{2} molecules. However, N\textsubscript{2} experiment in Fig. 1a also indicates that products Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2} are due to the chemical reactions of Rh\textsubscript{Al}O\textsubscript{2} with CO rather than collision-induced dissociation and Rh\textsubscript{Al}O\textsubscript{2}O\textsubscript{2} may oxidize five CO molecules consecutively (equation (1)).

\[
\text{RhAlO}_m + \text{CO} \rightarrow \text{RhAlO}_m^{1--15} + \text{CO}_2 \quad (m = 6--2) \quad (1)
\]

**Figure 1 | Reactivity of RhAlO\textsubscript{2}O\textsubscript{2} with CO.** Time-of-flight mass spectra for reactions of mass selected RhAlO\textsubscript{2}O\textsubscript{2} with N\textsubscript{2} (a,e,g) and CO (b,d,f,h) are shown. Peaks marked with asterisk and hollow circle in d are CO adsorption products of Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2} and Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2}, respectively. Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2} and Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2} (X = N\textsubscript{2}, CO and H\textsubscript{2}O) species are labeled as x,y,z and x,y,z,x, respectively. Signal 1,2,4H\textsubscript{2}O in h is due to the residual water in the gas handling system. The time periods for reactions Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2} + CO, Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2} + CO and Rh\textsubscript{Al}O\textsubscript{2}O\textsuperscript{2} + CO were about 1.1, 0.7 and 0.6 ms, respectively. The reactant gas pressures are shown in mPa.

**Figure 2 | Reactivity of RhAlO\textsubscript{2}O\textsubscript{2} with CO.** Time-of-flight mass spectra for reactions of mass selected RhAlO\textsubscript{2}O\textsubscript{2} with He (a), N\textsubscript{2} (c) and CO (b,d) are shown. The time period was ~ 0.6 ms for both reactions.

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[Image of the table and graph]
The strong signals that can be assigned as RhAl_2O_4CO^+ and RhAl_2O_3(CO)_2^+ (Fig. 1a–d) on the interaction of RhAl_2O_5^+ with CO, which is more facile than N_2 displacement (Fig. 1a), and further demonstrates the presence of O_2^•• or O_2^-unit in RhAl_2O_5^+. Each of the cluster source generated RhAl_2O_m^+ (m = 5–2) clusters could also react with CO to generate products, from RhAl_2O_5^+ to RhAl_2O_5^+ (Figs 1f,h and 2b,d). This provides convincing evidence that RhAl_2O_5^+ can indeed oxidize five CO molecules consecutively. The pseudo-first-order rate constants (k_1, in unit of 10^{-10} cm^3 per molecule per second) on the interaction of RhAl_2O_m^+ (m = 6–2) cluster ions with CO can be well fitted (Fig. 3) and the determined rate constants are presented in Supplementary Table 1. The rate constants for the reactions of the cluster source generated RhAl_2O_m^+ (m = 6–2) with CO are 4.9 ± 1.5 (m = 6), 6.2 ± 1.9 (m = 5), 1.6 ± 0.5 (m = 4), 6.9 ± 2.0 (m = 3) and 2.4 ± 0.7 (m = 2), which correspond to the reaction efficiencies of about (37 ± 11)%, (47 ± 14)%, (13 ± 4)%, (54 ± 16)% and (19 ± 6)%, respectively. Furthermore, we note that the clusters with odd number of oxygen atoms such as RhAl_2O_3^+ are more reactive towards CO oxidation than clusters with even number of oxygen atoms such as RhAl_2O_6^+.

**Reaction mechanism.** The density functional theory calculated thermodynamic data for CO oxidation by RhAl_2O_m^+ (m = 2–6) are shown in Fig. 4. The overall oxidation (RhAl_2O_m^+ + 5CO → RhAl_2O_9^+ + 5CO_2) is highly exothermic (−9.00 eV). The lowlying energy isomers of clusters RhAl_2O_m^+ (m = 6–1) are provided in Supplementary Figs 1–6. The lowest energy isomer of RhAl_2O_6^+ is in the triplet spin state (Supplementary Fig. 1) and contains a superoxide O_2^-• unit (O–O bond: 137 pm; Fig. 5). The existence of O_2^-• unit in RhAl_2O_6^+ is consistent with the appearance of RhAl_2O_4N_2^+ and RhAl_2O_4CO^+ (or RhAl_2O_4(CO)_2^+) on the interaction of RhAl_2O_6^+ with N_2 and CO (Fig. 1a–d), respectively. Supplementary Figs 7 and 8 show that the Al-site adsorption contributes to the displacement of the O_2^-• unit in RhAl_2O_6^+ by N_2 or CO and both reactions are calculated to be thermodynamically and kinetically favourable, and CO displacement is more facile than N_2 displacement. This is consistent with the relatively higher intensity of RhAl_2O_6^+ (natural charge: +1.14 e) can trap CO tightly at the first step (I1, ΔH_θ = −1.49 eV; Fig. 5; and then the oxidation of CO (I1 → TS1 → I2) by the highly reactive atomic oxygen radical.
anion O•− (ref. 31) takes place. Direct CO oxidation by the O2•− unit has to suffer from a positive barrier of 0.03 eV, which is much less favourable than the oxidation by O•−. The Rh atom in product RhAl2O5(+) (denoted as ⁷RhAl2O5•+), the structure of which is different from the lowest energy structure; Supplementary Fig. 2) can capture another CO tightly (I3, binding energy of −2.18 eV). Formation of the bent CO2 is the bottleneck (I3→TS2→I4) for CO oxidation by ⁷RhAl2O5•+. This step is to subject to a barrier of 1.26 eV. The subsequent steps follow a nearly downhill pathway characterized by small barriers to yield RhAl2O4(−) (Fig. 5) and then the O2•− unit in the experiment.

The key step for the transfer of five oxygen atoms from RhAl2O6•− to CO lies in the facile dissociation of the O2•− unit in ⁷RhAl2O5•−. Dissociation of the chemically adsorbed molecular O2 (superoxide O2•− or peroxide O22•−) is often considered to be the crucial step in oxidation reactions32. Recent gas-phase studies indicated that a single Au atom in AuTi3O8−23 is not enough to promote the dissociation of the O22•− unit, while the Au dimer in Au2VO4 can promote O22•− unit dissociation or direct participation in CO oxidation33. In this study, a single Rh atom in ⁷RhAl2O5•− can promote the dissociation of the O2•− unit and the process is much more favourable than CO2 desorption (Fig. 5). This is rationalized by the strong Rh–C multiple bonds (5.97 eV)33 and the strong Rh–O bond (4.16 eV)34. Thus, the Al–O2•− unit in I4 can approach the Rh atom favourably to form structure Al–O2−→−Rh–CO2 in I5. The elongation of the O–O bond from 1.37 pm in I4 to 1.47 pm in I5 is a good indicator for the activation of the superoxide O2•− to peroxide O22•− unit. The structure of I5 is crucial to induce further electron flowing into the O22•− unit from both of the Rh atom and the CO2 unit (Fig. 5), and then the O22•− unit can be dissociated favourably to produce O2−−Al–O2−−Rh–CO2 (I5→TS4→I6).

Direct oxidation of CO by the O2•− unit in ⁷RhAl2O5•− (Supplementary Fig. 9) is less favourable than the pathway in Fig. 5. This is consistent with previous study that instead of the direct participation in CO oxidation, molecular oxygen adsorbs at the interface between the oxygen vacancy and the single Rh site and then is followed by facile dissociation35. Release of three additional oxygen atoms from the resulting RhAl2O6•− to CO are calculated to be thermodynamically and kinetically favourable (Supplementary Figs 11–13). In each of these OAT steps, Rh atom functions as the preferred trapping site to anchor CO and then delivers CO for oxidation by the oxygen atoms in direct connection with Rh. The theoretical calculations well interpret the unique reactivity of RhAl2O6•− observed in the experiment.

**Discussion**

Metal-mediated OAT reaction is usually accompanied with the reduction of central metal by electrons that are stored originally in the removed oxygen atoms36 (equation (2)).

\[
M^{n+} + O_2 + R \rightarrow M^{(n-2)} + O_2- + RO
\]  

(2)
The positively charged metal centre is crucial to provide not only the characteristic site for the adsorption of CO (ref. 37) but also the oxidative centre to accept electrons. Recent gas-phase studies highlighted that the cleavage of Au–O bond and the formation of Au–M bond (M = Al, V, Ti, and Fe) is of great importance in CO oxidation by Au-doped clusters22–25. However, each of the Au-doped clusters can oxidize only one or at most two CO molecules and then the polarity conversion of Au atom from positive to negative takes place because of the formation of the reductive Au–M bond. In sharp contrast, natural charge analysis demonstrates that after the transfer of four oxygen atoms from RhAl2O5+ to CO, the Rh atom is still positively charged (+ 0.53e, Fig. 6) in product RhAl2O3+, which can also oxidize a CO molecule. The natural charge on Rh atom is decreased from +1.14e in RhAl2O5+ to +1.00e in RhAl2O3+ after the oxidation of the first CO. In this step, Rh acts as the primary centre to accumulate the electron that is localized originally on O,* radical, as shown from the change of spin density distribution, RhAl2O5+ versus RhAl2O3+. However, the Rh atom is re-oxidized in product RhAl2O3+ (+1.15e) after the oxidation of the second CO due to the dissociation of the O2* unit (14→15→16; Fig. 5). This step is crucial to recover the oxidative reactivity of Rh. In situ Raman spectroscopic study also demonstrated that supported Rh oxide can oxidize CO and then the Rh oxide is subsequently re-oxidized by the oxide atoms from oxide support.7 This phenomenon can be traced back to the well-fitting strength of Rh–O bond (4.16 eV)34, which is strong enough to promote the dissociation of the O2* unit in RhAl2O3+ and prevent the formation of the reductive Rh–Al bond (3.26 eV, by theoretical calculation) in RhAl2O3+ but at the same time is relatively weak to deliver oxygen atoms to oxidize CO (O–CO: 5.52 eV)38. Previous studies show that Rh prefers to coordinate not only with the surface oxygen atoms but also the subsurface oxygen in oxide support35. The strong Rh–O bond inhibits the migration of Rh atom to the oxygen vacancy and remains positively charged. Using high-resolution in situ X-ray diffraction and transmission electron microscopy, Stierle and colleagues1 reported the reversible and oxygen-induced shape transformation of Rh nanoparticles by the formation of O–Rh–O surface oxide during the cycle of catalytic CO oxidation. In contrast, the stronger Au–M (Au–Al = 3.37 eV (ref. 39), Au–V = 2.49 eV (ref. 38) and Au–Ti = 2.56 eV (by theoretical calculation)) than Au–O bond (2.27 eV)34 facilitates the formation of the reductive Au–M bond after the oxidation of only one or two CO molecules.

The negatively charged Rh has been theoretically predicted40 and experimentally postulated41. The RhAl2O+ cluster is a linear structure (Al–O–Al–Rh) and the single oxygen atom is sandwiched between two Al atoms. This structure with triplet spin state has been confirmed to be the lowest energy isomer of RhAl2O+ by more accurate CCSD(T) calculation (Supplementary Fig. 6). The two unpaired electrons are mainly localized on the Rh atom (~ 1.83 μB, Fig. 6), indicating that such Rh atom can be considered to be Rh<sup>–1</sup> (4d<sup>5</sup>5s<sup>1</sup>). The electron configuration calculations (4f<sup>8</sup>5d<sup>5</sup>6s<sup>1</sup>6p<sup>1</sup>) provide solid evidence for the negatively charged Rh in RhAl2O+. Thus, the oxidation state of Rh changes from +2.5 in RhAl2O5+ to −1 in RhAl2O (calculated based on the distribution of spin density; Fig. 6) during the transfer of five oxygen atoms from RhAl2O5+ to CO. This rather large range of Rh oxidation state changes in chemical reactions has rarely been reported (the Au oxidation state changes from +1 to −1), covering from cationic to anionic, and it is the driving force to accumulate the electrons that are stored originally in the released oxygen atoms and promotes the unique oxidative reactions to proceed.

In conclusion, we have demonstrated that a single atom of Rh can unexpectedly promote the transfer of five oxygen atoms to oxidize CO from a nine-atom cluster RhAl2O5+. This study leads a leap ahead towards OAT reactions in the field of cluster science and represents an important step to understand the participation of lattice oxygen promoted by noble metals. The preferable Rh–O rather than the reductive Rh–Al bond formation together with the capability of Rh to accumulate the large amounts of electrons are crucial factors to drive the unique reactions. This gas-phase study reveals the molecular-level origin for the puzzling experimental observation that trace amounts of Rh can promote the reactivity of lattice oxygen of Al2O3 (refs 4,5,9), a chemically very inert material.

Methods
Cluster generation and reactivity detection. The RhAl2O<sup>+</sup> cluster ions were generated by laser ablation of a mixed-metal disk compressed with Rh and Al powders (molar radio Rh/Al = 1/1) in the presence of O2 (0.4%) seeded in a He carrier gas with a backing pressure of 6.0 standard atmospheres. The cluster ions of interest were mass selected using a quadrupole mass filter and then entered into a linear ion trap (LIT) reactor, where they were cooled by collisions with a pulse of He gas and then interacted with a pulse of 5% (for reactions RhAl2O<sup>+</sup> (m = 2–5) + CO) or 2% (for reaction RhAl2O<sup>+</sup> + CO) CO seeded in He for around 0.6–1.1 ms. The temperature of cooling gas (He), reactant gases (CO or N2) and the LIT reactor was around 298 K. The cluster ions ejected from the LIT were detected by a reflector time-of-flight mass spectrometer. The details of running the time-of-flight mass spectrometer42, quadrupole mass filter43 and the LIT44 can be found in our previous works.

Rate constant fitting. Equation (3) was used to determine the pseudo-first-order rate constants (k<sub>i</sub>) of cluster reactions in an ion trap reactor45, in which I<sub>k</sub> is the signal intensity of the reactant cluster ions, I<sub>r</sub> is the total ion intensity including product ion contribution, f<sub>p</sub> is the Boltzmann constant, T is the temperature (~ 298 K), f<sub>p</sub> is the reaction time and P is the effective pressure of the reactant gas in the ion trap reactor.

\[
\ln \frac{I_r}{I_k} = -k_i \frac{P}{k_B T}
\] (3)

To calculate the reaction efficiencies (the possibilities of reaction on each collision), the collision rate constants were calculated on the basis of the surface charge capture model developed in the literature50. It is noteworthy that for reaction RhAl2O<sup>+</sup> + CO, the relative ion intensity of RhAl2O<sup>+</sup> is the reactive component generated in the experiment and the unreactive component is not included. The unreactive component of RhAl2O<sup>+</sup> could be well-fitted by equation (4)45.

\[
I_k = x_{unr} + (1-x_{unr}) \times \exp(-k_i \frac{P}{k_B T})
\] (4)

in which x<sub>unr</sub> is the relative intensity of the unreactive component of RhAl2O<sup>+</sup> and k<sub>i</sub> is the pseudo-first-order rate constant of the reactive component of RhAl2O<sup>+</sup>. The x<sub>unr</sub>, determined to be about 12%, indicating that the experimentally generated RhAl2O<sup>+</sup> may have isomers that are not or less reactive with CO.
Computational details. Density functional theory calculations using the Gaussian 09 (ref. 46) programme were carried out to investigate the mechanistic details on the oxidation of five CO molecules by a nine-atom–aluminum oxide cluster (RhAl10O36). To find an appropriate functional for the Rh–Al–O system, the bond dissociation energies of Rh–O, Rh–C, Al–O, O–O, Rh–Al, and O–CO were computed by various functionals and compared with available experimental data (Supplementary Table 2). It turns out that M06L is the best overall; thus, the results by M06L were given throughout the work. The TZVP basis sets48 for Al, C, and O atoms and a D95V basis set49 combined with the Stuttgart/Dresden relativistic effective core potential (denoted as SDD in Gaussian software) for Rh for RhAl10O36 were used. The relaxed potential energy surface scan was used extensively to obtain good guess structures for intermediates and transition states along the pathways. The transition states were optimized using the Beryn algorithm51. Intrinsic reaction coordinate calculations52 were performed so that each transition state connects two appropriate local minima. Vibrational frequency calculations were carried out to check that intermediates and transition state have zero and only one imaginary frequency, respectively.

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**Author contributions**

The original manuscript, figures, tables and the Supplementary Materials were prepared by X.-N.L. The theoretical calculations were prepared by H.-M.Z. and X.-N.L. The experimental data were prepared by Z.Y. and H.-M.Z. S.-G.H. provided the original idea, helpful discussions and the contribution in the manuscript revision.

**Additional information**

**Supplementary Information**

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