Rh single atoms on TiO₂ dynamically respond to reaction conditions by adapting their site

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Supported noble metal nanoparticles are widely investigated heterogeneous catalysts due to their high activity and selectivity for valuable products. However, the high prices and finite resources of these noble metals limit their applications in large-scale production. Heterogeneous single-atom catalysts (SACs), which consist of isolated atoms anchored onto supports, maximize the efficiency of noble metal utilization.\(^1\)–\(^5\) Moreover, developing catalysts that precisely place the single metal atoms homogeneously at a single site on the support can offer high selectivity towards a specific product. Thus, as a bridge between homogeneous and heterogeneous catalysis, SACs have become a new frontier in catalysis science and thus attracted significant attention recently.\(^6\)–\(^15\)

A single atom (SA) on a support possesses unique chemical and physical properties due to its particular local chemical environment, inducing an electronic structure that differs from that of conventional supported nanoparticle catalysts. However, the identification of this local environment of SAs under experimental conditions, as well as operando characterization of structural changes of SAs during catalytic reactions, is still challenging despite the development of in situ microscopy and spectroscopy techniques.\(^16\) The local environment determines the electronic structure, charge distribution, and oxidation state of the SAs, and hence also the stability, activity, and selectivity of the catalyst. Two main types of structures have been described for SACs: either substituting a cation at the oxide surface or supported on-top of the support, and these two types of SAs generally exhibit different catalytic properties.\(^17\) Camellone and Fabris\(^18\) reported that substitutional Au\(^{3+}\) ions at the ceria surface, and not supported Au\(^{+}\) adatoms, activate molecular CO and oxidize it to CO\(_2\). In the case of cobalt oxide (CoO)-supported Rh SACs, Rh substituted at the Co site was shown to be active and selective towards propene hydroformylation\(^19\), while Rh substituted at the Co site was shown to be active and selective towards a specific product. Thus, as a bridge between homogeneous and heterogeneous catalysis, SACs have become a new frontier in catalysis science and thus attracted significant attention recently.\(^6\)–\(^15\)

For each selected TiO\(_2\) surface termination, and each type of Rh addition, the stability of the various terminations, two oxygen-deficient ones (0.65 and 1.30 vacancies by nm\(^2\)) and one oxygen-rich one (0.65 additional O by nm\(^2\)), and we explored a large range of positions for the Rh atom, in substitution of a Ti atom (denoted as Rh\(_1@\)support) or supported on the surface (denoted as Rh\(_1@\)support), and of relative positions between the Rh atom and the vacancies/additional O. This allowed us to generate multiple environments and electronic structures for the Rh atom. The stability of the various terminations can be compared using first-principles atomistic thermodynamics, using oxygen chemical potential (\(\mu\)) as a descriptor (Ti chemical potential is then fixed from the bulk energy of TiO\(_2\)). For each selected TiO\(_2\) surface termination, and each type of Rh site (supported or substitutional), all Rh atom positions have been evaluated, but only the most stable one is considered in the surface stability diagram (Fig. 1). Other positions and their relative energies can be seen in Supplementary Figs. 1 and 2.

Under oxygen-rich conditions (high chemical potential of oxygen, \(-1.7 < \Delta\mu(O) < 0\)), Rh substituted at the 6-fold Ti site in the stoichiometric TiO\(_2\) (Rh\(_1@\)TiO\(_2\)) is the most favorable structure (Fig. 1a). Terminations with additional O atoms, and Rh appearing as a supported oxide moiety (Rh\(_1@\)TiO\(_2+x\)), are close in energy in the highest part of the interval, but never appear as most stable. Under oxygen-poor conditions, the stability of different Rh structures under typical experimental conditions with first-principles atomistic thermodynamics, in order to show how SAs dynamically respond to reaction conditions. Stabilization of SAC requires strong interaction between the metal atom and the oxide, and although several oxides have been shown to be adequate (Fe\(_2\)O\(_4\), TiO\(_2\), CeO\(_2\), Co\(_3\)O\(_4\), TiO\(_2\)), TiO\(_2\) avoids additional theoretical challenges linked with magnetic properties or relativistic effects. We experimentally characterize single Rh atoms on rutile after different reduction steps under hydrogen by CO probe molecule infrared (IR) spectroscopy and scanning transmission electron microscopy (STEM) imaging.\(^22\) The combination clearly demonstrates that Rh SAs change their structure and adapt their catalytic site under reaction conditions towards a structure active for CO reduction to CO under hydrogen by reverse water gas shift (RWGS).

**Fig. 1** Stability and structure of substitutional (\(\ominus\)) and supported (\(\forall\)) single-atom Rh. The TiO\(_2\)(110) surface is considered, including O vacancies or adatoms. **a** Relative stability as a function of oxygen chemical potential \(\Delta\mu(O)\). **b** The optimal structures for substitutional (\(\ominus\)) and supported (\(\forall\)) Rh SAs on the considered TiO\(_2\) surfaces. The structures in **b** and **c** follow the placement and order in the legend of **a**. Color code: O—red; Ti—blue; Rh—green.
with a decreased $\mu(O)$, one oxygen vacancy is formed, and initially the Rh atom remains in the substitutional site (Rh$_1$@TiO$_{2-x}$), the vacancy corresponding to a surface O atom bridging Rh and Ti. If $\mu(O)$ is further decreased below $-2.5$ eV, the most stable configuration shifts from the substituted model (Rh$_1$@TiO$_{2-x}$) to the supported model (Rh$_1$/TiO$_{2-x}$). The most favorable structure for this adsorbed Rh atom is above an O vacancy corresponding to a 3-fold subsurface oxygen, which is not the most stable vacancy position on the bare TiO$_2$ surface. Under typical conditions used during catalyst calcination (700 K in air, which is used to remove organic species deposited during catalyst synthesis), where $\Delta\mu(O)$ is calculated to be $-0.78$ eV, the substitutional structure is most favorable and the surface is stoichiometric. The local environment for Rh$_{1+x}$O$_{2-x}$ is Rh$_{1+x}$O$_{6}$ with a calculated Rh charge of $+1.84$ [e] and a formal oxidation number of Rh$(+4)$. A supported neutral Rh atom on stoichiometric TiO$_2$ (Rh$_{1}$/TiO$_{2}$) is $-3$ eV less stable. Two additional O atoms can stabilize the supported Rh as a cation (Rh$_{2}$/TiO$_{2}$), but this structure remains $1$ eV less stable than the substitutional cation site. Changing the temperature and O$_2$ partial pressure does not affect the preferred structure for Rh (Supplementary Fig. 3). Rh SAs always prefer to localize at the site of the oxide cation, suggesting that it tends to replace the metal cations in the oxides$^{1,25}$.

**Stability in H$_2$ reduction conditions.** Hydrogen can adsorb on the Rh atom or on the two-coordinated surface O atoms of TiO$_2$, and the optimal coverage at thermodynamic equilibrium depends on the H chemical potential $\mu(H)$ (Supplementary Fig. 4). Under a typical condition for H$_2$ reduction (0.1 atm H$_2$ at 500 K), where $\Delta\mu(H)$ is calculated to be $-0.35$ eV, a high coverage of H on the surface O atoms is reached with 7$H$ in the selected unit cell (containing 8 two-coordinated O atoms) for Rh$_{1}$/TiO$_{2}$ and Rh$_{1}$/TiO$_{2-x}$, and 6$H$ for the other structures (Rh$_{1}$/TiO$_{2-x}$, Rh$_{1}$/TiO$_{2-x}$ and Rh$_{1}$/TiO$_{2-x}$ respectively). The optimal hydrogenated structures are shown in Supplementary Fig. 5. Rh at a substitutional site is coordinated to six O atoms, and hence unable to bind H. O vacancies, created preferentially near the Rh, lead to unsaturation and 1 (resp. 2) H binds to the substituted Rh in the presence of 1 (resp. 2) vacancies. In a rather similar way, the supported Rh atom binds 2H atoms, if 1 or 2 O vacancies are present.

At the given $\mu(H)$ value, the relative stability for each model still depends on the chemical potential of oxygen, as shown in Fig. 2a, in a similar way to Fig. 1a. A major difference is that the high pressure of hydrogen drives the system into an O-poor condition. Under reduction conditions, hydrogen will react with surface O atoms to form water and if we assume an H$_2$ conversion of 0.01% to H$_2$O, and still 0.1 atm H$_2$ at 500 K, $\Delta\mu(O)$ is then fixed at the low value of $-3.23$ eV. At this O chemical potential, the substitutional and supported Rh atom structures have almost the same free energy (Fig. 2b) and hence both coexist at thermodynamic equilibrium. This supported Rh becomes stable vs. the substitutional cation upon the formation of two O vacancies around Rh, and in this situation, it is liganded to two H atoms. Therefore, Rh SAs on TiO$_2$ adapt their site from substitutional to supported when going from oxygen-rich preparation to H$_2$-reduction conditions. Mobility of the TiO$_2$ surface at high temperature under H$_2$ allows filling of the Ti vacancy formed after extraction of the Rh atom$^{18}$.

If $\Delta\mu(O)$ and $\Delta\mu(H)$ are independent, a 2D surface stability diagram can be constructed as a function of these two descriptors (Fig. 3). High $\Delta\mu(O)$ stabilizes the substitutional sites, and low $\Delta\mu(O)$ the supported sites, but the frontier between the stability regions of the two sites (shown as a thick black line) is moved towards lower $\Delta\mu(O)$ when $\Delta\mu(H)$ (and hence the H coverage) is increased, especially in the temperature region corresponding to reduction conditions (400–600 K). This trend is explained by the strong adsorption energy of H on Rh ($-2.30$ eV) in the presence of two O vacancies, which extends the stability of the green zone in Fig. 3. Hence, hydrogen pressure stabilizes both the substitutional and the supported site, but the shift to very O-poor conditions strongly favors the supported site, which becomes more stable.

**Stability under a pressure of CO.** Upon submitting the system to a pressure of CO, the preferred structure is governed by the O and CO chemical potentials. CO adsorbs on the supported SA and all possible adsorption sites for SA Rh with one or two CO adsorbed have been tested (Supplementary Fig. 7). The most

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**Fig. 2** Stability of single Rh atom on TiO$_2$(110) under a pressure of H$_2$. Substitutional (@) and supported (/) sites are compared. **a** Relative stability as a function of $\Delta\mu(O)$ under a typical condition of H$_2$ reduction (H$_2$ pressure of 0.1 atm at 500 K, i.e. $\Delta\mu(H) = -0.35$ eV). **b** Free energy for different Rh atom configurations in specific condition corresponding to water formation equilibrium ($\Delta\mu(H) = -0.35$ eV and $\Delta\mu(O) = -3.23$ (–3.33) eV for 0.01% (0.001%) conversion). The dashed line in a represents the condition (0.01% conversion) in b. **c** The local environment of Rh SAs in Rh$_{1}$/TiO$_{2-x}$, Rh$_{1}$/TiO$_{2-x}$, Rh$_{1}$/TiO$_{2-x}$, and Rh$_{1}$/TiO$_{2-x}$ (from left to right). Color code: O—red; Ti—blue; Rh—green. O vacancies are indicated by small dashed circles. Conversion fixes the pressure of H$_2$O. For instance, 0.01% conversion means a H$_2$O pressure of 10$^{-5}$ atm. Then $\mu(O)$ is obtained by $\mu(H_2O) - \mu(H_2)$.

**Stability under a pressure of CO.** Upon submitting the system to a pressure of CO, the preferred structure is governed by the O and CO chemical potentials. CO adsorbs on the supported SA and all possible adsorption sites for SA Rh with one or two CO adsorbed have been tested (Supplementary Fig. 7). The most
stable structure for each Rh site, TiO₂ termination, and CO coverage is chosen to establish the stability diagram. The complete 2D stability diagram, as a function of $\Delta \mu (O)$ and $\Delta \mu (CO)$, is shown in Fig. 4a. Partial diagrams constrained to one CO or two CO adsorption for a fixed $\Delta \mu (CO)$ value can be seen in Supplementary Fig. 8. Upon CO pressure, the zones corresponding to Rh being stable as a supported atom (purple in Fig. 4a) are strongly extended. This is especially the case for a typical condition of CO adsorption used in volumetric chemisorption or probe molecule IR experiments (a 10% gas mixture of CO, and 90% He at atmospheric pressure and room temperature), in which $\Delta \mu (CO)$ is calculated to be $-0.59 \text{ eV}$, a situation where the supported Rh is more stable than the substitutional one for the almost entire range of O chemical potential considered here (Fig. 4a and Supplementary Fig. 9). CO adsorption hence completely changes the thermodynamic site preference for the Rh

**Fig. 3** Surface stability diagram for Rh single atom on TiO₂(110) in the presence of H₂. Axes represent the H and O chemical potentials (noted $\Delta \mu (H)$ and $\Delta \mu (O)$ in eV). Different colors indicate the various configurations for the Rh and the TiO₂ surface, where blue, light blue, and green denote regions where Rh is preferentially substituting a six-coordinated surface Ti with zero, one, or two O vacancies (Rh₁@TiO₂, Rh₁@TiO₂−x, Rh₁@TiO₂−2x) and orange and pink zones where the supported Rh structure is favored (Rh₁/TiO₂−x and Rh₁/TiO₂−2x), respectively. The amount of hydrogen adsorbed on the TiO₂ surface and the Rh atom depends on $\Delta \mu (H)$ and dash lines limit the zones corresponding to different hydrogen coverage (see Supplementary Fig. 6). The red triangle (blue square) line shows the relation between $\Delta \mu (O)$ and $\Delta \mu (H)$ when water formation reaction is included with 0.01% (0.001%) conversion. $\Delta \mu (H)$ values for 0.1 atm H₂ and various temperatures are shown on the right vertical axis.

**Fig. 4** Structure and stability Of Rh single atom in the presence of CO. **a** Surface stability diagram for Rh single atom on TiO₂(110) as a function of CO and O chemical potentials. Colors indicate the different number of CO molecules adsorbed on Rh₁TiO₂, where orange, green, and purple represent the 0CO, 1CO, and 2CO, respectively. The temperature in right axis corresponds to the $\Delta \mu (CO)$ in left axis with 0.1 atom CO. **b** Local environment of Rh₁/TiO₂ in the presence of CO. **c, d** 3D (**c**) and 2D (**d**) representations of the charge density difference between 2CO/Rh₁/TiO₂ and Rh₁/TiO₂, show the donation and back-donation electron transfers.
atom, irrespective of the presence of O vacancies. This is explained by the fact that CO adsorbs significantly more strongly on the supported Rh (−4.89 eV for Rh1/TiO2), compared to the substitutional Rh (−2.74 eV for Rh1@TiO2−x). Charge density difference demonstrates that the strong interaction between Rh SAs and CO molecules results from not only Rh-C σ-bonding but also back-donation from the metal towards the antibonding ω CO orbital (Fig. 4c, d).

Hence thermodynamics under CO pressure tends to drive all Rh atoms to a supported site, if the temperature is high enough for kinetic aspects not to be limiting. Thus, the CO molecule plays a role in stabilizing the supported Rh SAs. Experimentally, CO is typically adsorbed on Rh after H2 reduction, so the surface is partially reduced by H2 with the formation of two oxygen vacancies and thus the most favorable structure under CO pressure should be 2CO/Rh1/TiO2–x.

To further illustrate the potential for Rh site modification of hydrogen or CO adsorption, we can define the driving energy of the transformation as the difference of free energy between the most favorable supported site and the most favorable substituted site, a negative driving energy indicating that the site change towards the supported case is thermodynamically favorable. During CO adsorption, the driving energy is markedly negative, with a value of −1.5 eV in the relevant region of chemical potential (see Supplementary Fig. 10b). This driving energy for site change is much stronger under a pressure of CO than under a pressure of H2, where it becomes negative only at very low μ(O) and remains close to energy neutral. This result further proves that CO and H2 molecules adapt the sites of SAs via different mechanisms and with different strength due to difference in their bonding mechanism.

Stability vs. cluster formation and FTIR studies. Thermo-dynamic analyses hence show that Rh SACs on TiO2 will adapt their sites in response to reaction conditions, such as under H2 or CO pressure. Beyond its position on the oxide, the stability of the SA vs. clustering is another key aspect, especially when it is in supported situation and hence has potential mobility. Our calculations show that under a pressure of CO (2CO/Rh/TiO2 structure), dimerization of the Rh(CO)2 species is less stable by 1.14 eV (Supplementary Fig. 11). Hence initial clustering of the SA is thermodynamically unfavorable. In addition, the Rh SA liganded to two CO is more stable than bulk Rh metal (Supplementary Fig. 9), precluding the formation of large nanoparticles. Similarly, under H2 reduction condition (6H/Rh/TiO2–x structure), the dimerization of the RhH2 surface species into a supported Rh2H4 unit is endothermic by 1.24 eV (Supplementary Fig. 11). However, in that case, the H-liganded Rh SA is less stable than bulk Rh (Fig. 2c). Since dimer formation is endothermic, the nucleation process is difficult, and the SA is metastable at reasonable temperature. There is hence a risk of particle formation only under H2 at high temperature.

In order to validate our conclusions, we synthesized Rh SAs on rutile TiO2 support, varied in situ pretreatments conditions, and used spectroscopy and microscopy to analyze the evolution of the Rh structure and TiO2 support. CO probe molecule IR experiments were executed at −120 °C, which allows us to kinetically trap the structure, avoiding any changes induced by the adsorption of CO. CO adsorption on Rh SAs supported on TiO2 has previously been shown to yield a specific doublet of peaks at −2097 and −2028 cm−1, associated with the symmetric and asymmetric stretches of the Rh(CO)2 gem-dicarbonyl species. Figure 5a shows the IR spectrum of CO adsorption at −120 °C on four differently in situ pretreated samples (oxidized at 350 °C, reduced at 100, 200, and 300 °C), to correlate with the predicted structures that would form in varying oxidation and reduction conditions. The pre-oxidized (350 °C in O2 for 1 h) sample does not adsorb CO at −120 °C. This is fully consistent with aforementioned calculation results, since during O2 pretreatment, O chemical potential is high (−0.61 eV) and Rh SAs are stabilized in a +4 oxidation state in the substitutional site of Ti (Rh1@TiO2), a situation where CO cannot adsorb on the Rh cation.

After reduction in H2 at 100 °C, CO adsorbs on Rh at −120 °C with a predominant stretch at 2094 cm−1 and a very small
accompanying stretch at 2026 cm$^{-1}$. The formation of a majority species with CO adsorbing to Rh atoms with a 1:1 stoichiometry agrees with calculations of the Rh@TiO$_2$–x species, which show preference for the adsorption of single CO with a vibrational frequency of 2071 cm$^{-1}$. This is consistent with the pathway followed in Fig. 3, where Rh@TiO$_2$–x forms due to exposure of Rh@TiO$_2$ species (that do not adsorb CO) to mild reduction conditions. Further reduction in H$_2$ at 200 °C induces the growth of the stretch at 2031 cm$^{-1}$ and a shift in the stretch at 2094 to 2097 cm$^{-1}$. This result is consistent with the calculations that predict the formation of the gem-dicarbonyl species 2CO/Rh$^{+}$/TiO$_2$–x, (Fig. 4b), and the calculated frequencies for CO are 2082 and 2023 cm$^{-1}$, in good agreement with the experimental values. However, when the reduction temperature is increased to 300 °C, one notes the appearance of a CO band at 2070 cm$^{-1}$, showing the agglomeration of Rh SAs in Rh clusters.

The primary conclusions of the CO probe molecule IR characterization were substantiated via ex situ atomic resolution STEM imaging of the Rh/TiO$_2$ sample following reduction in H$_2$ at 100 and 300 °C, see Fig. 5c, d and Supplementary Fig. 12. For the sample that had been reduced at 100 °C, single Rh atoms were primarily observed in all images. Alternatively, for the sample that had been reduced at 300 °C, a mixture of Rh clusters and SAs were observed. Both observations are in agreement with the interpretation of the CO IR characterization. It is interesting to note that while 300 °C reducing conditions in H$_2$ were observed to drive encapsulation of Rh particles by reduced TiO$_2$ overlayers (see Supplementary Fig. 13), the combination of CO IR and STEM imaging presented here suggests that single Rh atoms will not be encapsulated by TiO$_2$ under similar conditions.

When CO adsorption is performed at 20 °C, all three reduced samples show similar Rh(CO)$_3$ spectral features, suggesting that CO adsorption, when the temperature is high enough to allow atom mobility, drives Rh atoms to similar supported Rh(CO)$_2$ geometries, even though they may be in different starting locations, Fig. 5b. The small difference in the CO stretch frequencies likely derives from small differences in surface O-vacancy coverage on the TiO$_2$ support. From the sample pretreated at 300 °C, the feature at 2070 cm$^{-1}$ disappears after CO adsorption at 20 °C, showing that supported Rh particles can be readily fragmented to Rh SAs in the presence of CO, see Fig. 5b, in line with the calculated high stability of supported SAs in these conditions. This scenario is reminiscent of the dynamic SA formation during nanogold catalysis. As expected, the intensity of the symmetric stretch (~2090 cm$^{-1}$) at 20 °C is stronger than that of the asymmetric stretch (2023 cm$^{-1}$) for the Rh(CO)$_3$ species due to the existence of nearby O vacancies in TiO$_2$, but the exact ratio of intensity depends on reduction conditions.

It should be noted that for the pre-oxidized Rh sample, exposure to 20 °C CO does not change the properties at all, Fig. 5b, and in fact exposure to CO at 300 °C is required to induce O-vacancy formation that enables CO adsorption, see Supplementary Fig. 14. That is because the stable and highly coordinated substitutional site cannot provide an adsorption site for CO, so that CO is unable to interact and to transform the site to the supported structure. Hydrogen hence has a special role in creating O vacancies around the substitutional Rh cation, reducing its coordination and opening a channel for CO adsorption, and subsequent migration of the CO stabilized Rh species. The creation of oxygen vacancies when CO acts alone as a reductant at 300 °C is further evident because CO$_2$ was observed to form, presumably through oxidation by TiO$_2$ lattice oxygen, and these O vacancies in turn enabled the formation of Rh(CO)$_2$ species (Supplementary Fig. 14).

X-ray photoelectron (XPS) spectra showed a downshift of the XPS Ti 2p core level by 0.3 eV, from 459.0 to 458.7 eV, when comparing oxidation at 350 °C to reduction under hydrogen at 200 °C, indicating a reduction of some of the Ti in the sample, most likely at the surface of the oxide nanoparticle as indicated by the DFT calculations. Additionally, the O1s level in the reduced case is also downshifted by 0.4 eV, together with the appearance of a new feature at higher (+1.9 eV) binding energy (Supplementary Fig. 15). This peak is assigned to the formation of surface hydroxyls under hydrogen pressure. In addition, by using the integrated area of the Ti and O peaks and associated sensitivity factors, it was observed that the O:Ti ratio decreased by 5% after reduction. The XPS and IR results are in agreement with the DFT calculations, and that reduction of the Rh/TiO$_2$ catalysts induces hydroxylation and oxygen vacancy formation, which in turn drive the switch in the preferred Rh local coordination, enabling interaction with adsorbates.

Catalytic reactivity. In a nutshell, the combination of theory and experiment shows here that Rh atoms adapt their binding site to the presence of various reactants (O$_2$, H$_2$, and CO). It is hence important to explore whether this adaptive character has an impact on catalytic properties. We selected the RWGS reaction as an example for this purpose since when submitting a mixture of CO$_2$ and H$_2$ to a Rh on TiO$_2$ catalyst, it was shown that dispersed Rh SAs are active and selective for CO formation (from RWGS), while Rh nanoparticles lead to methanation.

Under reaction condition (500 K, 10 CO$_2$:1 H$_2$), 6H/Rh$^{+}$/TiO$_2$–x, and 6H/Rh$^{+}$/TiO$_2$–2x are the most favorable hydrogenated structures for substitutional and supported models, respectively (Supplementary Table 1). Hence, both structures were considered as initial state for the RWGS pathways and considering two mechanisms: via CO$_2$ dissociation or COOH-mediated. In the first case, the key step is the direct dissociation of CO$_2$ to CO, while for the second possibility, adsorbed CO$_2$ will react with surface OH species to form COOH that dissociates to OH and CO species. For the supported Rh atom structure 6H/Rh$^{+}$/TiO$_2$–x, the CO$_2$ dissociation path is the most favorable and the first step consists in forming a second O vacancy, necessary to activate CO$_2$. One of the two H on Rh reacts with a neighboring OH species, forming one water and one oxygen vacancy, with a barrier of 1.05 eV (Fig. 6 and Supplementary Table 2). Water easily desorbs at reaction temperature, creating a vacancy site where CO$_2$ can adsorb in an exergonic way, with an adsorption internal energy of −1.70 eV and a bent geometry, indicating a strong activation of CO$_2$ at this site. Then, the dissociation of CO$_2$ to CO occurs with a very low activation barrier (0.26 eV), the CO naturally coordinating to the Rh atom. The final steps (H$_2$ dissociative adsorption and CO desorption) occur easily, but the order is important since H$_2$ adsorption assists CO desorption. According to the energetic span model, the effective barrier of the reaction is 1.52 eV. In contrast, the reaction is much more difficult if one starts from Rh in substitution of Ti in 6H/Rh$^{+}$/TiO$_2$–2x. The Rh atom is saturated by two H atoms and, in order to create an adsorption site for CO$_2$, one H must be transferred to a nearby O atom (Supplementary Fig. 16, Supplementary Table 3). Reaction with a surface –OH species to form H$_2$O is not allowed here, since it is endothermic (+1.49 eV) with a barrier of 3.00 eV. Transfer to subsurface oxygen is still not favorable, with an endothermic energy of +1.46 eV and a barrier of 2.30 eV. Activation of the Rh center for RWGS is hence not possible, and the substitutional structure for the Rh atom is not catalytically active, because the strong adsorption energy of hydrogen on Rh prevents CO$_2$ adsorption. This indicates clearly that the active site for Rh SAC on TiO$_2$ in the case of the RWGS...
reaction is the supported site rather than the substitutional site. Further electronic structure analysis (see Supplementary Fig. 17) shows that Rh, liganded to two H atoms, is slightly negatively charged (−0.06 [e]) in 6H/Rh/TiO2−x and that its oxidation state is zero. In the unit cell, four protons and one vacancy provide six electrons. Five Ti3+ are located at the surface of the unit cell (representing 31% of surface Ti cations) and one electron is shared on the RhH2 unit. After creation of another vacancy by desorption of H2O (2v + 4H* intermediate on Fig. 6), one more Ti4+ is reduced to Ti3+ on the surface and Rh gains further electronic population (charge: −0.50 [e]). This negatively charged Rh can transfer electron to CO2, and promote the adsorption and activation of CO2.

The steady-state nature of the catalyst in reaction conditions is given by the most stable intermediate along the profile. For the supported Rh on TiO2, this corresponds to the coadsorption of CO and H on Rh, with three additional H adsorbates and one O vacancy on the TiO2 unit cell (Rh(H)(CO) in Fig. 6). In reaction conditions, it is 0.21 eV (Supplementary Table 1) more stable than the best substitutional site, which in the same conditions bears two H on the Rh and four H adsorbates and two O vacancy on TiO2. This Rh(H)(CO) structure is supported experimentally by in situ Fourier-transform infrared spectroscopy (FTIR) measurements under the same reaction conditions where a linear CO adsorption on SA is covered by H and CO and becomes catalytically active.

Further electronic structure analysis (see Supplementary Fig. 17) shows that the Rh species retained its SA structure (Supplementary Table 1). The rate controlling intermediate is the supported Rh(H)(CO) unit. Atom color code: O—red; Ti—blue; Rh—green

Fig. 6 Free energy profile of the RWGS reaction on the Rh single atom. The supported structure of the Rh atom 6H/Rh/TiO2−x, and the dissociation mechanism are considered. The first steps correspond to water formation and additional O-vacancy creation, followed by easy activation of CO2 forming CO. Color code: O—red; Ti—blue; Rh—green.
Our findings have provided insights on the critical questions of stability of heterogeneously supported SAs under reductive condition and the dynamic position changes of these atoms in redox reactions. The approach, and the proposed link between the transformation of the support and the restructuring of the metal, can in principle be extended to other SAC with similar metals (Rh, Pt, Ni, etc.) on reducible oxides (Fe₂O₃, CoO, CeO₂) in order to understand how the chemical nature of oxide and metal controls the restructuring process. The message from the present study is that as-prepared catalysts provide structures with the metal at high oxidation state occupying the oxide cation position, and that migration to a more reduced, supported and adequately liganded structure might be required for optimal catalytic activity. Our results provide a detailed understanding of the local structure of SAs on oxide support and their adaptive and dynamic character under realistic catalytic conditions, which are key insights that chemists should have in mind when designing single SACs.

Methods

DFT parameters. All the calculations were performed using periodic DFT methods implemented in the Vienna Ab initio simulation package (VASP) code. The projector augmented wave method was used for the interaction between the atomic cores and valence electrons. The valence orbitals of Ti (3d, 4s, 4p), Rh (4d, 5s), O (2s, 2p), C (2s, 2p), and H (1s) were described by plane-wave basis sets with cutoff energies of 400 eV. The exchange-correlation energies were calculated by the generalized gradient approximation with the Perdew–Burke–Enzerhof functional. Spin polarization was considered using unrestricted Kohn–Sham formalism. To correct the strong electron-correlation properties of these oxides, the DFT + U calculations were performed with \( U = 4.2 \) eV for Ti, which is taken from the literature.

The force threshold on each relaxed ion was set as 0.02 eV/Å. Monkhorst–Pack \( \Gamma \)–centered \( k \)-points grid sampling within the Brillouin zones were used according to the following equation: \( E_{\text{ads}} = E_{\text{slab}+\text{ads}} - E_{\text{slab}} - E_{\text{ads}} \), where \( E_{\text{slab}+\text{ads}} \) and \( E_{\text{ads}} \) are the electronic energy of species adsorbed on the surface, the bare surface, and the gas-phase molecule, respectively. Similarly, the desorption energy is defined as \( E_{\text{des}} = E_{\text{slab}+\text{ads}} - E_{\text{slab}} - E_{\text{ads}} \) and the reaction energy is defined as \( \Delta E = E_{\text{slab}+\text{ads}} - E_{\text{slab}} \). The charge density differences were evaluated using the formula \( \rho_{\text{B}} = \rho_{\text{A}} - \rho_{\text{X}} - \rho_{\text{Y}} \), where \( \rho_{\text{A}} \) is the electron density of X. Atomic charges were computed using the atom-in-molecule scheme proposed by Bader.

Stability descriptor. The system chemical potential \( \mu \) was used to measure the stability of different models with a consistent reference:

\[
\mu(\text{system}) = E(\text{system}) - n(O)\mu(O) - n(\text{TiO}_2)\mu(\text{TiO}_2) - (E(\text{TiO}_2) + \mu(\text{Rh})),
\]

where \( E(\text{system}) \) is the VASP calculated energy of Rh/\( \text{TiO}_2 \) structures, and \( E(\text{TiO}_2) \) is the energy of the bare \( \text{TiO}_2 \) surface. The \( \mu(\text{Rh}) \) and \( \mu(\text{TiO}_2) \) represent the chemical potential of bulk Rh and TiO₂, respectively, and \( \mu(O) \) is the free energy of oxygen atom. Bulk solid chemical potentials are taken from optimized DFT structures. The \( n \) values are set to balance the stoichiometry relative to a standard \( \text{Rh}/\text{TiO}_2 \) system, namely, the \( \text{TiO}_2 \) surface slab and bulk Rh. The relative free energy is calculated for each system by subtracting the energy of this standard system.

The chemical potential of oxygen atom, \( \mu(O) \), is calculated as a function of temperature \( T \) and oxygen partial pressure \( P_{\text{O}_2} \) using

\[
\mu(O) = 1/2(E(\text{O}_2) + \Delta\mu(\text{O}_2,T,P)),
\]

where \( \Delta\mu(O) \) is the value of \( \mu(O) \) when using the half of \( E(\text{O}_2) \) as zero reference. Similar definitions are used to \( \Delta\mu(H) \) and \( \Delta\mu(\text{CO}) \).

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Author contributions

Y.T. conducted DFT calculations and wrote the paper. C.A. and P.C. synthesized and characterized materials, and co-wrote the paper. M.L., G.G. and X.P. executed and analyzed STEM measurements. P.S. and J.L. designed the study, analyzed the data, and co-wrote the paper. All the authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.
