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Introduction

Supported rhodium catalysts show high activity for a number of reactions, including CO oxidation.^{1–4} It is generally accepted that Rh nanoparticles supported on rigid, irreducible substrates catalyze CO oxidation *via* the Langmuir–Hinshelwood (L–H) or Eley–Rideal (E–R) mechanisms, where the CO and O₂ molecules either coadsorb on the surface (L–H), or one of the molecules reacts directly from the gas phase with the other molecule adsorbed on the surface (E–R).^{6–12} However, the reactivity of the system is often affected by the choice of support, and reducible supports enable an alternative pathway, the so-called Mars-van-Krevelen (MvK) mechanism. Here, oxygen is extracted from the metal oxide lattice to oxidise CO, and the lattice is repaired by O₂ from the gas phase.^{14,16–19} Metal–support interactions are not always beneficial, however, and encapsulation by the support can completely deactivate the catalyst.^{13,14,20,21}

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Adsorbate-induced structural evolution changes the mechanism of CO oxidation on a Rh/ $Fe_3O_4(001)$ model catalyst⁺

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The structure of a catalyst often changes in reactive environments, and following the structural evolution is crucial for the identification of the catalyst's active phase and reaction mechanism. Here we present an atomic-scale study of CO oxidation on a model Rh/Fe₃O₄(001) "single-atom" catalyst, which has a very different evolution depending on which of the two reactants, O₂ or CO, is adsorbed first. Using temperature-programmed desorption (TPD) combined with scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), we show that O₂ destabilizes Rh atoms, leading to the formation of Rh_xO_y clusters; these catalyze CO oxidation *via* a Langmuir–Hinshelwood mechanism at temperatures as low as 200 K. If CO adsorbs first, the system is poisoned for direct interaction with O₂, and CO oxidation is dominated by a Mars-van-Krevelen pathway at 480 K.

Improving a catalyst's activity, selectivity, and stability requires the optimization of atomic-scale processes that are very difficult to ascertain on working catalysts. This motivates the use of welldefined model systems studied by the surface science approach, which can provide atomic-scale insights.

In this paper we present how CO oxidation proceeds on a Rh/Fe₃O₄(001) model "single-atom" catalyst. Using a combination of temperature-programmed desorption (TPD), scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS), we show the system is active for CO oxidation by both L-H and MvK mechanisms, depending on which of the reactants the surface is exposed to first. Oxygen adsorption leads to formation of superoxo $(O_2)^-$ species bound to Rh₁ adatoms, which rapidly agglomerate to small Rh_xO_v clusters. The clusters contain weakly bound oxygen, which reacts with CO below room temperature. In contrast, CO adsorption on the bare Rh₁ species poisons the system for O₂ adsorption, but CO oxidation nevertheless takes place via a MvK mechanism at ca. 480 K. Two different deactivation mechanisms are observed: the oxidised clusters become inactive after the first desorption of the weakly bound oxygen, while the Rh₁ adatoms incorporate into the support lattice as the CO desorbs.

Methods

The experiments were carried out using two independent ultra-high vacuum (UHV) setups. The STM data were acquired

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in a two-vessel UHV chamber consisting of a preparation chamber ($p < 10^{-10}$ mbar) and an analysis chamber ($p < 7 \times 10^{-11}$ mbar) equipped with an Omicron μ -STM operated at room temperature in constant-current mode with electrochemically etched tungsten tips. The chamber further includes commercial XPS, Auger electron spectroscopy and low-energy electron diffraction instruments. The STM images were corrected for distortion and creep of the piezo scanner as described in ref. 22.

The TPD and XPS data were acquired in a second chamber equipped with a liquid-He cryostat, a home-built molecular beam source, a quadrupole mass spectrometer (Hiden HAL 3F PIC), a monochromatized Al/Ag twin anode X-ray source (Specs XR50 M, FOCUS 500), a hemispherical analyzer (Specs Phoibos 150), a low-energy electron diffraction setup (Specs ErLEED), an ion source (Specs IQE 12/38) and a UV source (Specs UVS 10/35). This chamber was specifically designed for surface chemistry studies of single-crystal oxide samples; full details are given in ref. 23. The samples were mounted on a Ta sample plate using Ta clips, with a thin Au foil placed between the sample plate and the sample to ensure good thermal contact. The sample plate was attached to the liquid-He cryostat via Ta rods, and the temperature was measured by a K-type thermocouple spot-welded on the sample plate. A molecular beam is formed by expansion of 0.53 mbar ¹⁸O₂ or 0.27 mbar ¹³CO through two differentially pumped stages. This results in a well-defined beam spot on the sample surface with a diameter of 3.35 ± 0.17 mm and a top-hat intensity profile.²³ The TPD spectra were acquired with a 1 K s^{-1} heating ramp.

All the experiments were conducted on natural Fe₃O₄(001) single crystals (SurfaceNet GmbH or Surface Preparation Laboratory) prepared by sputtering (1 keV Ar⁺ or Ne⁺, 10 min) and annealing in UHV (930 K, 10 min). Every other annealing step was done in a partial pressure of O₂ ($p_{O_2} = 5 \times 10^{-7}$ mbar, 20 min) to avoid reduction of the surface. Rhodium was deposited using Focus e-beam evaporators, and the deposition rate was calibrated by temperature-stabilized quartz crystal microbalances (QCM). One monolayer (ML) is defined as one atom per ($\sqrt{2} \times \sqrt{2}$)R45° unit cell of the Fe₃O₄(001), which corresponds to 1.42 × 10¹⁴ atoms per cm².

Results

Rh₁ species on Fe₃O₄(001)

Fig. 1a and b shows STM images of the $Fe_3O_4(001)$ surface before and after deposition of Rh. The undulating rows running in the [110] direction correspond to 5-fold coordinated Fe atoms in surface octahedral sites (Fe_{oct} , see model in the inset of Fig. 1a). In each pair of neighbouring terraces, the surface Fe_{oct} row direction is rotated by 90°, as expected for the spinel structure (not shown here). Surface oxygen atoms are not visible in the STM images because they possess no density of states near the Fermi level, but their positions are precisely known from diffraction studies and density functional theory calculations.^{24,25} This $Fe_3O_4(001)$ surface reconstruction is based on subsurface cation vacancies (therefore it's referred to as the SCV reconstruction), and it has



Fig. 1 Characterization of the Rh/Fe₃O₄(001) system by STM. (a) STM images of pristine Fe₃O₄(001) surface show undulating rows of Fe_{oct} running in the [$\tilde{1}10$] direction. The small bright species on the Fe_{oct} rows are surface hydroxyls.⁵ The inset shows a model of the Fe₃O₄(001) surface with the octahedral Fe_{oct}, tetrahedral Fe_{tet} and O atoms being represented by dark blue, light blue and red spheres, respectively. (b) After deposition of 0.2 ML Rh at room temperature, the majority species are Rh₁ adatoms (red circles), but we also observe slightly elongated species which we identify as Rh₂ dimers (cyan circles). (c and d) The Rh₂ dimers exhibit characteristic hopping motion in subsequent STM images (broken lines for guidance). (e and f) Scanning with a +3 V bias results in dissociation of the Rh₂ dimers (cyan arrows in panel e) into pairs of single Rh₁ adatoms (paired cyan arrows in panel f). The +3 V scan was done between acquisition of images shown in (e) and (f).

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been shown previously to support dense arrays of single metal atoms, preventing the adatom mobility and cluster formation even at elevated temperatures.^{15,24,26-28} This is due to the existence of highly stable adsorption sites with a nearest-neighbour distance of 0.84 nm, in which the adatoms are 2-fold coordinated to the surface oxygen atoms, essentially occupying a bulk continuation tetrahedral site (schematic representation shown in the uppermost inset of Fig. 2a). After deposition of Rh at room temperature, isolated Rh₁ adatoms appear as bright protrusions (red circles in Fig. 1b) sitting between the Fe_{oct} rows. In addition to the single Rh₁ adatoms, we also observe larger elongated species (cyan circle in Fig. 1b), which in subsequent STM scans exhibit a distinctive hopping motion over the adsorption site (Fig. 1c and d). We identify these species as metastable Rh₂ dimers that can be split into two Rh₁ adatoms by bias pulsing or high-bias scanning. Fig. 1e and f shows this process on two STM images acquired on the same spot: in Fig. 1e two Rh2 dimers are observed (cyan arrows), Fig. 1f shows pairs of isolated Rh₁ adatoms (smaller paired arrows) appearing instead of the Rh₂ after the surface was scanned with a +3 V bias. The observed hopping of the Rh₂ is restricted to the given adsorption site, thus it might be also considered a restructuring of the dimer and does not lead to destabilization of the system by diffusion or agglomeration. Apart from the dimer hopping, no mobility of Rh species is observed in subsequently acquired STM images at room temperature under UHV conditions. The Fe₃O₄(001) surface supports the Rh₁ adatoms even at significantly higher coverages; Fig. S1[†] shows an STM image of 0.5 ML Rh/Fe₃O₄(001) featuring a high density of Rh₁ adatoms, and XPS spectra acquired on an Fe₃O₄(001) surface with varying Rh coverage between 0.1

and 0.8 ML Rh showing virtually no difference in Rh 3d peak shape or position.

At elevated temperatures, the Rh₁ adatoms are unstable against incorporation into the $Fe_3O_4(001)$ support. Such a phenomenon has been observed for several different metal adatoms on Fe₃O₄(001) before and the foreign adatom can either substitute a 5-fold coordinated surface Feoct or incorporin the vacant octahedral site of the SCV ate reconstruction.^{13–15,29} Schematic representations of the three possible sites of Rh1 near the surface are shown in insets in Fig. 2a. The incorporation of Rh takes place at temperatures above ≈ 450 K and can be followed both in STM and XPS, as shown in Fig. 2a and b. STM images taken after annealing to 500 K show predominantly elongated (orange circle) and circular (purple circle) features on the Fe_{oct} rows, which is consistent with Rh1 incorporated into the subsurface 6-fold site or surface 5-fold site, respectively (STM simulations of different metal adatoms in the same sites are provided in ref. 14, 15 and Fig. S2[†]). Additionally, we observe an increased number of bigger brighter features, presumably Rh clusters, and a very small number of remaining 2-fold Rh1 adatoms (red circle). Fig. 2b shows the Rh 3d region of XPS spectra taken after depositing 0.6 ML Rh and heating to different temperatures. After deposition at 300 K, the Rh 3d peak maximum is located at ≈ 307.7 eV, but its broad shape suggests convolution of several components. Apart from the main signal corresponding to 2-fold Rh₁, the additional XPS components might come from the Rh₂ dimers or Rh₁ adatoms residing in the vicinity of surface defects or step edges. On different samples, small variations of the peak maximum between 307.7 and 308.1 eV were observed, most likely depending on the relative



Fig. 2 Rh₁ adatoms incorporate into the Fe₃O₄(001) support upon annealing above 450 K. (a) STM images after deposition of 0.4 ML Rh and heating to 500 K show predominantly circular protrusions (highlighted by purple colour) and elongated protrusions (orange colour) on the Fe_{oct} rows. Only a very small number of Rh₁ remain in the 2-fold coordinated site between the Fe_{oct} rows (red colour). We identify the new species as Rh₁ incorporated in the octahedral cation sites near the surface, consistent with previously reported studies of various metal adatoms on Fe₃O₄(001).^{14,15} Schematic representations of these sites are shown in the insets and labelled with the color of the corresponding circle. (b) Rh 3d region of the XPS spectra (monochromatized Al Kα, grazing emission) taken after heating to different temperatures (measured after cooling back to 300 K). Upon heating to 400 K the Rh 3d peak maximum shifts to 308.0 eV, as the low binding-energy shoulder at 307.2 eV decreases. Heating above 450 K leads to an increase of the 309.5 eV component, which becomes dominant above 600 K. We attribute this component to Rh incorporated into the octahedral sites of the Fe₃O₄(001) surface. (c and d) The Fe 2p and O 1s peaks corresponding to the first and last spectra shown in (b). Notably, in the Fe 2p region the shoulder at ≈708.5 eV slightly increases upon Rh deposition, indicating an increased amount of Fe²⁺ near the surface. This shoulder decreases again upon heating as the Rh cations diffuse into deeper layers.

number of these species. After heating to 400 K we observe a decrease on the low-binding-energy side of the peak (around \approx 307.2 eV) and the peak maximum shifts to 308.0 eV. Heating above 450 K leads to an increase of a higher-binding-energy component at 309.5 eV and decrease of the signal at 308.0 eV. After heating to 650 K, the 308.0 eV peak is no longer observed, and the 309.5 eV component is dominant. Prolonged heating above this temperature leads to a decrease and eventual disappearance of the Rh signal in XPS, consistent with diffusion of Rh into the Fe₃O₄ bulk (Fig. S3[†]). Thus, we attribute the 309.5 eV component to Rh incorporated into the Fe₃O₄(001) substrate.

The Fe 2p and O 1s regions only show small differences with Rh deposition and heating (Fig. 2c and d). Upon Rh deposition, an Fe 2p shoulder at \approx 708.5 eV slightly increases in comparison to the clean surface, indicating an increased amount of Fe²⁺ near the surface.³⁰ This shoulder decreases again upon heating, presumably because the Rh incorporates and thus the number of near-surface cations decreases.

Exposing Rh₁/Fe₃O₄(001) to O₂

When the Rh₁/Fe₃O₄(001) system is exposed to O₂ at room temperature, the Rh₁ adatoms become mobile and begin to agglomerate. Fig. 3a–c shows three frames of an STM movie acquired while keeping a constant background pressure of 2 × 10^{-10} mbar O₂ in the analysis chamber. Single adatoms (highlighted by red circles) form well-resolved oxidised Rh₂O_x dimers (yellow rectangles) and subsequently bigger Rh_xO_y clusters (purple rectangle). Over the course of the STM movie, no O₂ adsorption was observed on the Rh₂ dimers (cyan circle).



Fig. 3 STM of Rh₁/Fe₃O₄(001) and its interaction with oxygen. (a–c) Three frames from an STM movie acquired while keeping a constant O₂ background pressure of 2×10^{-10} mbar. Panel (a) shows a majority of single Rh₁ adatoms (red circles). During the O₂ exposure these species first form well-resolved Rh₂O_x clusters (yellow rectangles in panels (b) and (c)) and subsequently bigger nanoparticles (purple rectangle in panel (c)). (d) After a high dose (50 L) of O₂ at room temperature the imaging becomes unstable, and the majority species are larger bright clusters of varying size and shape. A few Rh₁ adatoms remain; one of them is highlighted by the red circle.

After dosing a higher amount of O2 in the preparation chamber (50 Langmuir, where 1 L = 1.33×10^{-6} mbar s), the majority species observed in STM are small Rh_xO_v clusters, although some adatoms remain (Fig. 3d). Scanning of the oxidised Rh_xO_y species is difficult because the tip is very unstable, with frequent tip changes suggesting the presence of weakly bound species that interact with the STM tip. A comparison of the cluster density following saturation exposure with the initial adatom coverage suggests that the majority contain at most 2-3 Rh atoms. The fact that similar Rh agglomeration was observed after O₂ exposure in the preparation chamber suggests that the mobility observed in STM movies is not solely tip-induced. After heating the surface with oxidised Rh_xO_y clusters to 400 K, no structural differences are observed, but the imaging becomes much more stable, suggesting desorption or trapping of the weakly bound species.

Fig. 4a shows O_2 TPD measurements from the clean $Fe_3O_4(001)$ surface (grey curve) and from the surface with 0.6



Fig. 4 Spectroscopic characterization of O2 adsorption on Rh/ Fe₃O₄(001) by TPD and XPS. In all spectra, 1.5 L O₂ was dosed at 60 K. (a) O₂ TPD spectra acquired in the first (orange curve) and second (brown curve) dosing on 0.6 ML Rh/Fe₃O₄(001). Notably, the δ peak at \approx 330 K appears only in the first dosing experiment. Reference spectra of the clean surface are plotted in grey. (b and c) Details of the O 1s and Rh 3d XPS regions (monochromatized Al Kα, grazing emission) of 0.6 ML Rh/ Fe₃O₄(001) after O₂ dosing and heating to different temperatures. Compared to the pristine Fe₃O₄(001), we identify two new components in the O 1s region at 533.7 and 536.9 eV. The spectra taken after heating above room temperature look identical to the orange curve taken at 300 K. The whole O 1s region is shown in the inset in (b). (c) Adsorption of O_2 at 60 K causes a ≈ 0.9 eV shift of the Rh 3d peak, and a further shift is observed upon heating to 300 K. Heating above \approx 500 K leads to growth of the 309.5 eV component corresponding to Rh incorporated into the substrate. Up to 300 K, the spectra were taken at the temperatures given; for higher temperatures, the spectra were taken after cooling the sample back to 300 K.

ML Rh (orange and brown curves). On the pristine $Fe_3O_4(001)$ surface, O_2 physisorbs below 70 K (desorption peak labelled α in Fig. 4a, full spectrum shown in Fig. S4[†]), but in our work this phase could not be saturated due to the O₂ dosing temperature (60 K) being within this desorption peak. Thus, desorption already takes place before the start of the heating ramp and the magnitude and shape of the α peak varies in repeated measurements due to slightly varying time between dosing and heating. Above 100 K, the O2 TPD acquired on the pristine surface exhibits two distinct peaks, labelled β and γ in Fig. 4a and Fig. S4,† which presumably correspond to desorption from defects, domain boundaries, and/or step edges. The presence of Rh₁ adatoms on the surface prior to O₂ dosing leads to an increase of these two desorption peaks and induces a sharp new desorption peak, δ , at \approx 330 K. When the TPD measurement was repeated on the same sample (following termination of the previous heating ramp at 570 K), the δ peak was no longer present (brown curve in Fig. 4a), and a similar result was observed in a separate experiment when the first heating ramp ended already at 380 K, before any Rh incorporation took place (evidenced by XPS spectra).

XPS characterization of the O₂ adsorption on Rh/Fe₃O₄(001) is shown in Fig. 4b and c. Spectra taken directly after Rh deposition at 200 K and dosing 1.5 L O2 at 60 K reveal two new components in the O 1s region at 533.7 and 536.9 eV (red curve in Fig. 4b). The 536.9 eV signal quickly decreases over time and completely disappears within several minutes, which is consistent with the O_2 physisorbed on Fe₃O₄(001) and readily desorbing at 60 K. The 533.7 eV component remains unchanged upon heating to 105 K, but disappears upon heating above 250 K (blue and orange curves in Fig. 4b). After heating to 300 K (orange curve), the spectrum in the O 1s region closely resembles the spectrum acquired on a pristine Fe₃O₄(001) surface (grey curve), save for a very small and broad shoulder between 530-535 eV, which can be attributed to a small amount of water adsorbed on surface defects.³¹ Upon heating to higher temperatures up to 730 K, no significant change is observed in the O 1s region.

The adsorption of O_2 can also be followed in the Rh 3d region. Fig. 4c shows spectra taken after Rh deposition (0.6 ML),

dosing O₂ at 60 K, and heating to different temperatures. Directly after Rh deposition at room temperature the shape of the Rh $3d_{5/2}$ peak has a maximum at ≈ 307.7 eV, but as mentioned previously, its shape suggests convolution of several components. A small shoulder at ≈309.5 eV corresponds to Rh incorporated in the octahedral sites of the support (see Fig. 2); this component can be minimized by depositing Rh at lower temperature (Fig. S5^{\dagger}). After dosing O₂ at 60 K, the maximum of the Rh $3d_{5/2}$ peak shifts by ≈ 0.9 eV to 308.6 eV. Heating to 300 K induces a further shift to \approx 309.0 eV, and this position remains the same with heating to 400 K. At this temperature, a small shoulder at 308.2 eV appears. Heating above 460 K causes growth of the 309.5 eV component corresponding to incorporated Rh and slight increase of the signal at 308.2 eV. Above 700 K only the signal from the incorporated Rh remains. The Fe 2p region does not show any significant changes with O_2 adsorption and heating (spectra shown in Fig. S6[†]). The question of how the changes in XPS spectra correlate to the O2-induced Rh1 agglomeration observed by STM is covered in the discussion section.

Exposing Rh₁/Fe₃O₄(001) to CO

The same experimental approach as utilized above for O_2 was used to study CO adsorption on the Rh1 adatoms. Fig. 5 shows five frames of an STM movie recorded while keeping a background pressure of 5×10^{-9} mbar CO in the analysis chamber. In panel (a), the vast majority of the Rh₁ species have an apparent height of ≈180 pm (red circle). Over the course of the movie, the apparent height of the individual Rh₁ species abruptly decreases to 95-125 pm (panels b-d) and eventually almost all of the Rh₁ appear darker (panel (e)). We attribute this change to the formation of monocarbonyl RhCO, and the reduction of the apparent height to the modification of empty Rh states near the Fermi level through the interaction with CO. With higher doses of CO, we also observe double-lobed species oriented perpendicular to the surface Fe rows, which we assign as Rh(CO)₂ dicarbonyls (orange arrow in Fig. 5e and Fig. S7†). Noncontact atomic force microscopy (ncAFM) measurements of the Rh carbonyls acquired with a CO-terminated tip (Fig. S7†) appear strikingly



Fig. 5 Adsorption of CO on the Rh₁/Fe₃O₄(001) followed by STM. In panel (a), acquired in UHV, the vast majority of the Rh₁ adatoms (red circle) have an apparent height of \approx 180 pm. (b–d) During exposure in 5 × 10⁻⁹ mbar CO, the individual Rh₁ change their apparent height one by one to \approx 95–125 pm. We identify these as Rh₁(CO) species. (e) After a CO dose of \approx 10 L, the majority of Rh₁ are darker. The images also show a few double-lobed features (orange arrow), which we attribute to Rh₁(CO)₂ dicarbonyls. Detailed images of these species are shown in Fig. S5.†

similar to those observed in the previously published study of $Ir_1/Fe_3O_4(001)$,¹⁴ and one would indeed expect similar behavior for these two metals. As in the Ir case, the concentration of the dicarbonyl species never exceeded 25% of the total, which we attribute to the low pressures used in our experiments. Neither the monocarbonyls nor dicarbonyls appear to interact with molecular O_2 , as no changes were observed upon subsequent O_2 exposure in room-temperature STM measurements.

In ¹³CO TPD experiments on 0.5 ML Rh/Fe₃O₄(001), we observe a ¹³CO desorption peak with a maximum at \approx 530 K, which has an additional shoulder at \approx 450 K (Fig. 6a). Comparison to the spectrum acquired on the pristine Fe₃O₄(001) reveals that all the desorption signal above 250 K is



Fig. 6 TPD and XPS characterization of CO adsorbed on Rh/ Fe₃O₄(001). (a) CO desorbs from 0.5 ML Rh/Fe₃O₄(001) in a peak with a maximum around 530 K. A smaller signal of CO₂ is observed peaking around 480 K. (b) Adsorption of CO at 60 K on 0.6 ML Rh/Fe₃O₄(001) shifts the Rh 3d photoemission peak maximum to 308.5 eV, but heating to 300 K shifts the maximum to 308.2 eV. With annealing to temperatures above 500 K, a new component develops at 309.5 eV, due to Rh incorporated into the Fe₃O₄(001) support. (c) In the C 1s region of the XPS spectra, adsorption of CO at 60 K results in a dominant feature at 290.6 eV, corresponding to CO adsorbed at the Fe₃O₄(001) surface,³² and a smaller peak at 287.3 eV, corresponding to CO adsorbed on the Rh species. The 287.3 eV component is still observed after heating to 450 K. Above this temperature, no C 1s signal is observed in XPS.

related to Rh, and that the presence of Rh leads to disappearance of a defect-related ¹³CO desorption peak at \approx 190 K. On Rh/Fe₃O₄(001), a small ¹³CO₂ signal is observed at \approx 480 K, which we attribute to CO oxidation *via* a Mars-van-Krevelen mechanism. This phenomenon has been observed for Ir single atoms and Pt clusters on Fe₃O₄(001).^{14,18} No CO desorption is observed above 580 K and in XPS spectra the C 1s region is featureless after heating to these temperatures (Fig. 6c). The CO desorption features below 200 K in the TPD spectra correspond to CO adsorption on the clean $Fe_3O_4(001)$ surface.³² Focusing on the Rh 3d and C 1s regions of the XPS spectra, CO adsorption at 60 K induced a shift of the Rh 3d peak maximum to 308.5 eV accompanied by the emergence of C 1s peak components at 290.6 eV and 287.3 eV. The 290.6 eV peak corresponds to adsorption of CO on the bare $Fe_3O_4(001)$ surface.³² Heating to 300 K leads to desorption of CO from $Fe_3O_4(001)$, so that only CO bound to the Rh species remains (287.3 eV component in the C 1s region). The Rh 3d peak maximum shifts to lower binding energy (308.2 eV), and this position stays constant upon heating to higher temperatures. After the CO desorption from the Rh species above ≈ 500 K, the majority of the Rh incorporates into the surface, clearly evidenced by the increase in intensity of the component at 309.5 eV. Repeated ¹³CO TPD measurements feature a small desorption peak at \approx 410 K (Fig. S8[†]), which we attribute to CO desorption from Rh1 substituting an Fe atom in the 5-fold surface site. The Fe 2p region of the XPS spectra taken after CO adsorption and heating to different temperatures shows the same shape as the spectra taken without the CO (see Fig. 2c and Fig. S6†).

Sequential dosing experiments

Sequential ¹³CO and ¹⁸O₂ dosing experiments were performed to find out whether the Rh adatoms or Rh_xO_v clusters can coadsorb CO and O₂. Fig. 7a-d shows the CO (red) and CO₂ (blue and orange) signals desorbing from a 0.5 ML Rh/Fe₃O₄(001) sample exposed to CO and O₂ at different temperatures and in a different order. The blue area corresponds to CO₂ formed via a MvK mechanism $({}^{13}C{}^{16}O_2$, mass 45), while the orange area indicates CO₂ formed by a L-H mechanism (¹³C¹⁶O¹⁸O, mass 47). The corresponding ¹⁸O₂ signal (mass 36) acquired simultaneously is shown in Fig. S9.† Fig. 7a provides a reference in which the sample was saturated by ¹³CO at 300 K. Dosing O₂ on the sample predosed with ¹³CO at 130 K (panel b) leads to a lower CO desorption signal, and the overall amount of CO₂ produced is increased. The CO₂ signal produced via a MvK mechanism is comparable to the previous case, but additionally we observe a low, broad ¹³C¹⁶O¹⁸O signal between 200–500 K corresponding to CO_2 formed by a L-H mechanism. Overall, roughly 35% of the CO₂ produced is formed by the L-H channel.

The situation changes dramatically when the same gases are dosed with the order reversed (panel c). Dosing the ${}^{18}O_2$ before the ${}^{13}CO$ at 130 K leads to a significantly enhanced mass 47 signal, which now exhibits a clear maximum at \approx 340 K. The sum of masses 29, 45 and 47 is however signifi-

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Fig. 7 Probing the reactivity of 0.5 ML Rh/Fe₃O₄(001) by TPD after sequential dosing of ¹³CO and ¹⁸O₂. Red traces correspond to ¹³CO, blue areas to ¹³C¹⁶O₂ produced *via* a MvK mechanism and orange areas correspond to ¹³C¹⁶O¹⁸O produced *via* a L-H mechanism. (a) Dosing ¹³CO at 300 K results in spectra comparable to Fig. 6a. (b) Dosing ¹³CO at 130 K, then ¹⁸O₂ at 130 K leads to a lower ¹³CO desorption signal, but overall higher ¹³CO₂ production below 400 K. (c) Dosing ¹⁸O₂ first at 130 K, then ¹³CO at 130 K leads to significant CO₂ signal produced by the L-H mechanism, the MvK channel is suppressed. (d) Dosing ¹⁸O₂ at 300 K, then ¹³CO at 130 K leads to similar results as (c), but with more CO₂ produced above 400 K in both reaction channels.

cantly reduced compared to the previous CO-first experiments, which suggests that, overall, less CO can adsorb on the system once it is saturated with O₂ at 130 K, but a significantly higher proportion of adsorbed CO is converted to CO2. The overall amount of CO₂ produced is comparable to the case shown in Fig. 7b, but now the majority ($\approx 60\%$) forms via the L-H channel. If the system is predosed with O₂ at 300 K prior to CO adsorption, the observed CO₂ TPD signal shown in Fig. 7d is significantly enhanced between 400 and 500 K in both reaction channels. In this experiment the amount of formed CO_2 is the highest (\approx 35% higher than in the previous two cases), and approximately 50% is formed by the L-H channel. These experiments, with O₂ predosing at 130 and 300 K, likely differ in that the oxygen-induced Rh₁ diffusion should be suppressed at low temperature, and additional oxygen is bound at sites linked to Rh species (see Fig. 4a). No CO₂ formation by any mechanism is observed in the absence of Rh species (see Fig. S10[†]).

Discussion

The experimental data acquired on the Rh/Fe₃O₄(001) model catalyst clearly show that Rh₁ adatoms sinter rapidly when exposed to O₂ at room temperature, forming small Rh_xO_y clusters that are active for CO oxidation. Given the extremely low O₂ pressure used in the STM movies, it seems likely that just

one O₂ molecule is sufficient to create a mobile oxidised Rh species, probably Rh1O2. This suggests that oxygen adsorption significantly weakens the interaction of the Rh adatom with the support. DFT calculations for oxygen adsorption on the Rh₁/Al₂O₃ system predict significant electron transfer from Rh to O_2 , and the formation of superoxo $(O_2)^-$ species.³ In the O 1s XPS data taken after O2 adsorption below 100 K (Fig. 4b) we do observe a peak at 533.7 eV, which is close to the position expected for superoxo species.³³ However, this peak disappears after heating above 250 K, suggesting a further reaction with Rh takes place. We also observe a strong positive binding energy shift in the Rh 3d XPS peak maximum (Fig. 4c) after O_2 dosing at 60 K (308.6 eV), which shifts further to \approx 309.0 eV upon heating above 250 K. Even though the position observed at 60 K is already close to that expected for RhO_2 (308.6 eV)³⁴ or Rh₂O₃ (308.3 eV),^{34,35} and thus could be already interpreted as a signal corresponding to the oxidised Rh clusters, the further shift above 250 K accompanied with the disappearance of the superoxo component in the O 1s region suggests that the agglomeration takes place between 100 K and 250 K, and the O 1s signal of the resulting Rh_xO_y nanoparticles is indistinguishable from that of the O^{2-} in the Fe₃O₄ support.

Our room-temperature STM movies of O_2 exposure (Fig. 3a–c) suggest that the mobile Rh_1O_2 species interact strongly with bare Rh adatoms to form a well-defined double protrusion (presumably with Rh_2O_2 stoichiometry). The addition of yet another mobile Rh_1O_2 seems common, and would in principle

vield clusters of nominal Rh₃O₄ stoichiometry. These clusters appear larger, and have a scratchy appearance due to the interaction with the STM tip. The cluster density observed following 50 L O_2 exposure suggests that the clusters rarely grow larger than 2-3 Rh atoms, but it cannot be concluded how many O₂ molecules can ultimately be adsorbed on each cluster, nor whether the formation of these clusters results in the abstraction of one or more O atoms. Nevertheless, the O2 TPD measurements clearly show that some of the O atoms are weakly bound, and desorb as molecular O2 just above room temperature in the absence of CO (Fig. 4a). The Rh 3d spectrum is barely changed by this desorption; only a very small shoulder appears at ≈ 308.2 eV (green curve in Fig. 4c), which suggests the clusters remain oxidised. This shoulder gets significantly more pronounced after heating to 460 and 575 K (purple and cyan curves in Fig. 4c), and at the same time the component corresponding to incorporated Rh appears (309.5 eV). In the TPD spectra there is no O2 desorption signal observed above 380 K (up to 660 K, where the acquisition was stopped), therefore it seems likely that the oxygen from Rh_xO_y clusters gets accommodated in the Fe₃O₄ lattice as the Rh incorporates, and the 308.2 eV component in this case indicates an intermediate step between Rh_xO_v on the surface and Rh incorporated in the lattice. Repeating the oxygen exposure (after its desorption at \approx 350 K, but before the Rh incorporation at higher temperatures) does not replenish the weakly bound O₂, suggesting that the clusters restructure to a stable configuration, and that the weakly bound oxygen was a consequence of the agglomeration process.

When the O₂-sintered sample is exposed to CO at low temperature and TPD is performed, CO2 is found to evolve from the sample in a broad signal between 200-500 K (Fig. 7d). Isotopic labelling of the reactants shows that the majority of the CO₂ formed below ≈ 400 K is produced by the L-H channel, with the molecular O_2 being the oxidising agent. The observation of a similar result when the initial O₂ exposure was performed at 130 K instead of 300 K hints that O2-induced sintering happens already at low temperatures. Interestingly, the CO₂ signal at higher temperature is reduced in intensity when the O₂ exposure is performed at 130 K. The comparison of these two datasets suggests that the oxygen bound above 300 K (δ peak in Fig. 4a) is facilitating the CO₂ formation by the L-H channel, and the oxygen adsorbed below 300 K likely blocks a small number of sites for CO adsorption. An alternative explanation is that at 300 K the ¹⁸O₂ spills over to the Fe₃O₄ surface, which leads to the increased CO2 production above 400 K. In this case the process would be MvK, but due to the previous spillover from Rh it would be measured in both ¹³C¹⁶O₂ and $^{13}C^{16}O^{18}O$ signals. Reexposing the surface to O₂ following CO₂ desorption is not expected to facilitate further CO₂ production *via* a L-H mechanism, because the remaining Rh_xO_v clusters seem to be inert for further interaction with O_2 .

When the $Rh_1/Fe_3O_4(001)$ sample is exposed to CO first, the Rh adatoms do not become mobile at room temperature. We have recently shown that CO adsorption allows Ir_1 adatoms to achieve highly-stable square-planar environments,¹⁴ and our

STM/ncAFM images for Rh₁ (Fig. S7[†]) appear very similar. In ref. 14, the enhanced stability was rationalized by analogy to Ir(1) complexes, and it seems reasonable to expect similar behavior for Rh(I), which can also adopt the preferred square planar d⁸ configuration. The XPS spectra acquired on the COsaturated Rh/Fe₃O₄(001) system show almost no change in the Rh 3d region when heated to temperatures between 300 K and 450 K, suggesting most of the Rh carbonyls still exist at 450 K, and are still present before the CO_2 production takes place via a MvK mechanism at ≈480 K. Exposing the CO-saturated sample to O₂ does not lead to visible changes in STM or XPS, nor does it lead to significant low-temperature CO₂ production. We conclude that CO poisons the Rh adatoms for O2 adsorption, at least under our low-pressure conditions. We thus do not form OCOO species, which have been proposed as possible intermediates in prior studies of CO oxidation by Rhbased single-atom catalysts.^{36,37} This could be because the Rh atom is inaccessible to the O2 molecule once the CO is present, or because adsorbing both molecules on the same Rh adatom is energetically unfavourable. The situation could be different at higher pressures where the kinetic limitations are more easily overcome. A more likely scenario, however, is that stable Rh(CO)₂ dicarbonyls would be formed and the catalyst would remain poisoned for CO oxidation via a L-H mechanism. Our TPD experiments show that a small amount of CO is oxidised to CO₂ at high temperature via a MvK mechanism, but this is followed by immediate incorporation of Rh into the support, which ultimately deactivates the catalyst.

Conclusions

This study presents an atomic-scale view on a range of phenomena relevant for heterogeneous catalysis by single atoms and sub-nano clusters. We show that O₂ adsorption initially leads to formation of superoxo species bound to Rh₁ adatoms, which already at room temperature rapidly agglomerate to small Rh_xO_v clusters. CO adsorption, on the other hand, completes the preferred square-planar coordination environment of the Rh₁ adatoms, stabilizing the Rh₁ in place while poisoning them for O_2 adsorption. Both the oxidised Rh_xO_y clusters and Rh₁CO carbonyls show activity for CO oxidation, but via very different pathways: oxidised clusters catalyse the reaction via a Langmuir-Hinshelwood mechanism at temperatures as low as 200 K, while the presence of Rh carbonyls at 300 K allows CO₂ formation via a Mars-van-Krevelen mechanism at \approx 480 K. These results highlight the importance of a careful characterization of the catalyst during the exposure to the reactants and show that the gas composition can play a crucial role in the structural evolution of the catalyst.

Conflicts of interest

There are no conflicts to declare.

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