Anionic Single-Atom Catalysts for CO Oxidation: Support-Independent Activity at Low Temperatures

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Supporting Information

ABSTRACT: We study 14 atomically dispersed transition metals on halite-type oxides (MeO, Me = Fe, Mg, Mn, and Ni) using periodic density functional theory calculations and probe structure and activity toward CO oxidation for a subset of these systems experimentally. Pd and Pt can form stable negatively charged species upon binding to oxygen vacancies; the magnitude of the metal atom binding energy depends on the O vacancy formation energies of the supporting metal oxide and the lattice match between transition metal and support. The resulting oxide-supported single-atom systems catalyze CO oxidation by molecularly adsorbed O2 with intrinsic barriers as low as 36 kJ/mol for Pt/MnO(001). This high activity stems from the single sites’ ability to stabilize surface superoxide species. Furthermore, intrinsic barriers were found to depend primarily on the identity of the transition metal and to be nearly independent of the support identity. However, O2 may heal the oxygen vacancy, which leads to catalyst deactivation. Catalyst deactivation by oxygen can be suppressed by using a more reducible support such as FeO(001) or MnO(001).

KEYWORDS: atomic dispersion, density functional theory, CO oxidation, oxides, single-atom catalyst

1. INTRODUCTION

For catalytic applications, transition metals are typically dispersed on the surface of a less expensive support, as this decreases the percentage of inaccessible bulk metal atoms. The catalytic activity of these supported metal particles generally depends on their size.1–3 Atomically dispersed catalysts, or single-atom catalysts, are particularly desirable systems. Because of their uniform active sites, single-atom catalysts provide superior selectivity.4 These advantageous properties are responsible for an increase in research interest in this topic in recent years (e.g., refs 5 and 6).

Among other support materials, metal oxides such as Al2O3,11 CeO2,12–15 CuO,15 Fe2O3,16–19 Fe3O4,20 MnO2,21 and MgO22–24 have been used for the synthesis of single-atom catalysts. For most of these systems, the transition metal atoms bind to O ions, though Abbet et al. were able to stabilize single Pd atoms inside the O vacancies of MgO.22,23 Upon removing a neutral O atom from MgO, the two excess electrons localize in the now vacant O lattice position, forming an F0 center. Pd atoms binding inside F0 centers of MgO were found to enable CO oxidation at temperatures below 260 K, but the Pd atoms agglomerate upon CO2 formation, leading to catalyst deactivation.23

Small Au clusters (n < 20) supported on O-defective MgO catalyze the oxidation of CO at similar temperatures (240 K).25 This high activity is the result of an electron transfer from the F0 center to the Au d orbitals.26 Using density functional theory (DFT), Li and co-workers27 studied CO oxidation catalyzed by late transition metal atoms supported in F0 centers of MgO. They report CO oxidation barriers as low as 25 kJ/mol (Ag/MgO3), but they do not address the stability of their single-atom catalysts.

Using periodic DFT calculations, we study CO oxidation on transition-metal atoms supported on the (001) surface of MeO (Me = Fe, Mg, Mn, and Ni). While previous studies28–31 have highlighted the role of surface OH species for low-temperature CO oxidation, this study focuses on O2 activation at low temperatures. We find that Pd and Pt can form thermodynamically favorable single sites inside O vacancies; the magnitude of the metal atom binding energy depends on the oxygen vacancy formation energy and the lattice constant of the supporting metal oxide. On the basis of these predictions, three Pt/MeO catalysts (Me = Fe, Mg, and Mn) were prepared
experimentally. Pt atoms inside O vacancies were identified on the basis of their characteristic CO stretching mode at 1997 cm\(^{-1}\) in the infrared spectrum. Importantly, single-atom catalysts supported on metal oxides are not stable under CO oxidation conditions, which is in agreement with previous experimental work.\(^{33}\) Therefore, oxides with moderate vacancy formation energies such as FeO or MnO are predicted to be more suitable support materials for atomically dispersed Pd and Pt catalysts. For Pt atoms supported on MgO, MnO, and FeO, sintering was observed experimentally at temperatures around 336, 348, and 366 K, respectively, which is in good agreement with the predictions from DFT.

2. METHODS

2.1. Computational. Calculations were performed using the projector augmented wave (PAW) method\(^{32,33}\) as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^{34,35}\) Exchange-correlation energies were obtained using the functional by Perdew, Burke, and Ernzerhof (PBE).\(^{36}\) The onsite Coulomb correlation of occupied d orbitals was effective Hubbard-type parameters of 4.0 eV (Fe and Mn) and 6.3 eV (Ni); these values are derived in refs \(^{39}\) and \(^{41}\), respectively. The implementation of DFT+U follows Dudarev et al.\(^{42}\) A plane wave cutoff of 600 eV was used. Structure optimizations were performed until total energies were converged to 10\(^{-6}\) eV, and forces acting on the relaxed ions were below 0.02 eV/Å. Transition state structures were obtained using the improved dimer method.\(^{43,44}\) VESTA was used to visualize structures.\(^{45}\)

Vibrational frequencies were obtained by diagonalizing a partial, mass-weighted matrix of second derivatives with respect to the three Cartesian degrees of freedom of each atom. This “Hessian” matrix was proven by finite differences of the gradients with displacements of ±0.015 Å (central differences). Structures were proven to be minima by the absence of imaginary frequencies. For transition-state structures, one imaginary frequency was obtained.

The (2 × 2) surface unit cells were obtained by cutting the bulk oxides in (001) orientation. Optimized lattice constants (Table 1) are in good agreement with the values reported in

| Table 1. Local Magnetic Moments \(m\) [\(\mu_B\)] of Cations, Lattice Constants \(a\) [Å], Surface Energies \(\gamma\) [J/m\(^2\)], and Oxygen Vacancy Formation Energies \(\Delta E_{\text{def}}\) [kJ/mol] from eq 1 for the (001) Surfaces of the Oxide Supports Considered in This Work |
|-----|-----|-----|-----|-----|
| \(m\) | \(a_{\text{PBE}(U)}\) | \(a_{\text{exp}}\) | \(\gamma\) | \(\Delta E_{\text{def}}\) |
| FeO | 3.7, 3.7 \(^a\) | 4.39 | 4.29 \(^c\) | 0.62 | 301 |
| MnO | 4.6, 4.6 \(^b\) | 4.52, 4.48 \(^b\) | 4.44 \(^c\) | 0.63 | 424 |
| NiO | 1.8, 1.7 \(^c\) | 4.24, 4.20 \(^c\) | 4.19 \(^c\) | 0.83 | 437 |
| MgO | 0 | 4.26, 4.26 \(^c\) | 4.20 \(^c\) | 0.89 | 582 |

\(^a\)ref 39, \(^b\)ref 40, \(^c\)ref 41, \(^d\)ref 46, \(^e\)ref 47.

\(\Delta E_{\text{def}} = E(\text{Me}_{40}O_{40}) - E(\text{Me}_{40}O_{38}) - 1/2E(O_2)\) (1)

2.2. Experimental Section. 2.2.1. Catalyst Synthesis. Pt/MeO\(_x\)-SiO\(_2\) catalysts (0.1 wt % Pt and 10 wt % Me, Me = Mg, Mn, Fe) were prepared by wet impregnation method. The precursor, Mg(NO\(_3\))\(_2\)·6H\(_2\)O (99.0%; Sigma-Aldrich), Mn-(NO\(_3\))\(_2\)·4H\(_2\)O (>97.0%; Sigma-Aldrich), or Fe(NO\(_3\))\(_3\)·9H\(_2\)O (99.999%; Sigma-Aldrich), was dissolved in 3 cm\(^3\) doubly deionized water (>18 MΩ cm). The solution was added dropwise to a 7 cm\(^3\) suspension containing 3 g of SiO\(_2\) under constant stirring at ambient temperature. The suspension was stirred for another 12 h at ambient temperature and then dried at 393 K in the oven for 12 h. The solid support was heated to 823 K at 2 K/min for 4 h in flowing dry air (Linde, GR 0.1).

The "as-prepared catalyst" was synthesized as follows: the Pt precursor (H\(_2\)PtCl\(_6\)·6H\(_2\)O, Sigma-Aldrich, 99.9% trace metal bases) was dissolved in 1 cm\(^3\) deionized water; this solution was added dropwise to 4 cm\(^3\) of a liquid suspension containing the support powders (1 g) and doubly deionized water (4 cm\(^3\), > 18 MΩ cm) at ambient temperature. The suspension was stirred continuously for 12 h and then dried at 353 K for 12 h before heating at 2 K/min to 673 K for 2 h under flowing dried air (Linde, GR 0.1).

2.2.2. CO and H\(_2\) Uptake. CO chemisorption studies were carried out using a customized volumetric adsorption–desorption apparatus at 303 K. For each experiment, 300 mg of catalyst powder were loaded into a quartz sample holder. The catalyst was reduced with 10% H\(_2\) (Linde, 99.999%) in He (Linde, 99.999%) at a flow rate of 50 mL/min while the temperature was increased to 473 K. Then, the reactor was evacuated under dynamic vacuum (10\(^{-5}\) Pa) at 473 K for at least 12 h and cooled to 303 K. After this pretreatment, 5% CO (Linde, certified standard) was introduced to the sample in small increments (5 to 20 μmol per dose) until the CO partial pressure inside the reactor, which was measured by a pressure transducer (MKS, 120AA Baratron), increased to 0.4 kPa. For H\(_2\) uptake tests, the same procedure was used, except the CO/He mixture was replaced with H\(_2\) (Linde, 99.999%). The chemisorption experiments were repeated after the temperature-programmed CO oxidation experiments to study Pt sintering during the reaction.

2.2.3. Infrared Measurements. In situ Fourier-transform infrared spectroscopy (FTIR) was carried out using a Bruker Vertex 70 equipped with a mercury cadmium telluride (MCT) detector in transmission mode using an environmental cell equipped with KBr windows and a K-type thermocouple, which is mounted onto the sample holder and connected to a temperature controller. Prior to each experiment, the catalyst powder was pelletized into a thin disk (~1.3 cm diameter and ~25 mg/cm\(^2\) surface density) and placed in the sample holder. The inlet gases were controlled by mass flow meters (Brooks, SLAS850). Infrared spectra were taken between 500 and 4000 cm\(^{-1}\) at 296 K with a resolution of 0.40 cm\(^{-1}\), averaging over 16 scans at 0.40 cm\(^{-1}\) intervals.

For each experiment, the catalyst disk was first exposed to 10% H\(_2\) (Linde, 99.999%) in He (Linde, 99.999%) at a flow rate...
of 50 mL/min. The sample was heated to 473 K at 0.5 K/min and sequentially held at 473 K for 0.5 h. After that, the disk was cooled to 296 K and exposed to 2% CO (Linde, certified standard) in He (Linde, 99.99%) for 10 min at a flow rate of 50 mL/min, after which the absorbance features remained unchanged with time. The cell was then purged with He (Linde, 99.99%) at a flow rate of 50 mL/min for 0.5 h to remove gaseous CO before measuring the absorbance spectrum. To study the oxidation of preadsorbed CO, 10% O₂ (Linde, 99.99%) was introduced into the cell at a flow rate of 50 mL/min for 30 min at 296 K before measuring the absorbance spectrum.

### 2.2.4. Evaluation of CO Oxidation Rates

CO oxidation experiments were carried out with a U-shaped quartz reactor connected to a gas chromatograph (SRI-GC) equipped with a methanizer and FID detector. Prior to the reactivity testing, the samples were pelletized and sieved to 80–120 mesh. Catalysts (50 mg) were loaded into the reactor and pretreated with 10% H₂ (Linde, 99.999%) in He (Linde, 99.99%) at a flow rate of 50 mL/min at 473 K for 0.5 h before they were cooled to ambient temperature under flowing He. The temperature-programmed reaction was carried out between 303 and 473 K with a heating rate of 0.5 K/min. The feed gas, which contains 0.4 kPa CO (Linde, certified standard) and 10 kPa O₂ (Linde, 99.99%) with balance He (Linde, 99.99%), was introduced to the reactor at 100 cm³/min. The chemical composition of the effluent stream from the reactor was analyzed with a gas chromatograph at sampling intervals of 3 min. Turnover frequencies (TOF) refer to the number of CO molecules converted per second and are normalized by the total number of Pt atoms.
3. RESULTS AND DISCUSSION

3.1. Insights into Metal–Support Interactions from DFT. We find that transition metal atoms (m) bind preferably atop O ions on the pristine oxide surfaces. On the reducible oxides (i.e., FeO, MnO, and NiO), the O–m axis is slightly tilted toward a neighboring cation. This has been previously reported by Janik and co-workers, who found that the binding energies (BE) were correlated with, among other factors, the electron affinity (EA) of the metal and the O vacancy formation energy of the supporting oxide. However, binding energies calculated relative to bulk metal atoms (m_{bulk} in eq 3) are positive at θ = 1/8 (Table S2), which indicates that the formation of metallic particles is thermodynamically favored over atomic dispersion.

\[
BE = E(m/Me_{40}O_{40}) - E(Me_{40}O_{40}) - E(m_{bulk})
\]

Calculated binding energies for metal atoms inside O vacancies are less positive for all transition metals except Mn, which has a negative electron affinity. Transition metals with low electron affinities (Cr, Fe, and Mo) bind only to O vacancies with high defect formation energies. However, only the binding energies for Au, Pd, and Pt inside O vacancies are negative (Figure 1a). Based on the difference between the binding energies on pristine and O-defective oxide surfaces (Table S2), it requires more than 100 kJ/mol to move a Pd or Pt atom from an O vacancy onto a terrace site.

The strong binding of Au, Pd, and Pt atoms to O vacancies of MeO(001) is the result of a charge transfer from the defect states into the energetically lower metal states, which has been previously reported for MgO-supported transition metals.50 On MgO, this leads to Bader charges of −0.75 (Au), −1.53 (Pd), and −1.65 (Pt) for the transition metal atoms (Table 2). For the reducible oxide supports (FeO, MnO, and NiO), lower Bader charges were obtained for Pd and Pt, indicating a less pronounced charge transfer compared to the nonreducible MgO support.

The energy gain of the electron transfer depends on the energy difference between the corresponding orbitals. Thus, O vacancies with high-energy defect states, i.e. high vacancy formation energies ΔE_{dφ} bind transition metals more strongly. This is qualitatively different from the adsorption on pristine oxide surfaces, where binding energies of metal atoms are more exothermic on reducible oxides. The energy level of the acceptor states, on the other hand, depends on the electron affinity EA of the transition metal. While binding energies of metal atoms in the O vacancies of MeO(001) were found to correlate with both properties, an additional structural component is needed to reproduce binding energy trends. The descriptor \( d = (a_{MeO}/a_m)^3 \times (EA + ΔE_{dφ}) \), where \( a_m \) and \( a_{MeO} \) are the lattice constants of metal and metal oxide, respectively, correctly predicts binding energy trends following FeO < NiO < MnO ≈ MgO with a mean absolute error of 7 kJ/mol; the fit for Pd and Pt is shown in Figure 1b, and the underlying data is compiled in Table S3. While the descriptor utilizes the lattice constant of the transition metal (\( a_m \)), it refers to the binding of a negatively charged metal species in the O vacancy. The charge transferred to the metal atom upon adsorption leads to an increase in size, which is why an \( a_{MeO}/a_m \) ratio greater than 1 actually enhances the binding interaction between MeO and m. The descriptor also predicts that Pt does not form stable single-atom catalysts inside O vacancies of CeO₂(111), a support material with a lower vacancy formation energy (199 kJ/mol in ref 51) than any oxide considered in this work. This is in good agreement with results by Fabris and co-workers.13

While these calculations demonstrate that atomic dispersion of Au, Pd, and Pt is more stable than the formation of extended particles on the four oxide surfaces (with the exception of Au/FeO₂ see Figure 1a), one has yet to show that atomic dispersion is also more stable than cluster growth at the O vacancies. For Pd and Pt dimers at O vacancies, binding energies per metal atom are significantly less exothermic than the values for single atoms, as no additional charge transfer occurs. While larger clusters might be more stable than dimers, this indicates that particle formation is hindered by large barriers. Thus, atomic dispersion is favorable at low coverage, which is in good agreement with experimental findings in ref 23. For Au dimers, the binding energy per metal atom is similar to the value for the first atom. This would lead to a statistical cluster size distribution even at low coverage, which is in good agreement with previous DFT results in ref S2.

Interestingly, DFT binding energies for single atoms of Pd (218 kJ/mol) and Pt (288 kJ/mol) on pristine MgO(001) are similar to values extrapolated from experimental data by Hemmingson and Campbell, that is, 279 kJ/mol for Pd and 323 kJ/mol for Pt. They approximate the chemical potential of metal atoms in supported hemispherical nanoparticles using eq 4, where \( γ \) is the surface energy of the metal nanoparticle, \( E_{adh} \) is the adhesion energy between particle and support, \( V_n \) is the molar volume of the transition metal, and \( D \) is the effective diameter of the particle.

\[
μ - μ_{bulk} = (3γ - E_{adh})2V_m/D
\]

The chemical potential for Pt atoms in hemispherical nanoparticles supported on MgO(001) is plotted in Figure 1c (black line) using experimental values for \( V_n \) (9.09 × 10⁻⁷ m³/mol), \( γ \) (2.52 J/m²), and \( E_{adh} \) (1.51 J/m²) from ref 54. The effective diameter for the Ptₓ particles was calculated using \( D = \sqrt{1/6n}_r \), where \( r_s \) is the atomic radius of Pt (135 pm). This equation is derived by equating the volume of \( n \) Pt atoms and the volume of a hemisphere with diameter \( D \). Binding energies obtained in this work using PBE (black circles in Figure 1c) are close to the values predicted by eq 4.

However, binding energies for Pt clusters inside O vacancies (red circles in Figure 1c) are poorly approximated by eq 4. Qualitative agreement can be achieved by adding an additional term \( C/D^3 \) (eq 5; red line in Figure 1c for \( C = 16 \) kJ m⁻³/mol, value obtained by fitting to DFT data), which represents a stronger binding for the first Pt atom. Since the number of metal atoms scales with \( D^3 \), this stabilizing interaction has to scale with 1/\( D^3 \). This modification does not significantly affect the chemical potential for nanoparticles with \( D > 1 \) nm (more than 25 atoms), but it introduces a local or global minimum corresponding to atomic dispersion depending on the value of \( C \).

\[
μ - μ_{bulk} = (3γ - E_{adh})2V_m/D - C/D^3
\]

On the basis of these DFT results, we conclude that Pd and Pt can form stable single-atom catalysts inside the O vacancies of metal oxides. Binding energies were found to depend on O vacancy formation energies and the lattice match between transition metal and support. Because of their higher electron
affinity, Pt-based catalysts are predicted to be more stable than the Pd/MgO catalyst reported by Landman and co-workers.\textsuperscript{23}

### 3.2. CO Oxidation Activity: Insights from DFT

On the basis of DFT calculations, Li and co-workers\textsuperscript{27} concluded that the CO oxidation on metal atoms supported on O-defective MgO(001), denoted here as m/MgO, is mediated by a Langmuir–Hinshelwood mechanism. In this work, the same mechanism is adopted, but reaction energies and barrier heights were found to be different, because Li and co-workers\textsuperscript{27} did not allow for surface relaxation. Other oxidation pathways with even lower barriers may be feasible on the reducible oxide supports. Thus, barriers reported in this section represent an upper bound for the overall CO oxidation barriers. However, this upper bound already indicates low-temperature oxidation activity. In this section, CO oxidation on Pt/MgO(001) will be discussed in detail, but similar intermediates were obtained for the other single-atom catalysts considered in this work.

CO and O\textsubscript{2} adsorb on the Pt atom of M\textsubscript{0} (Figure 2) with individual adsorption energies of −113 and −43 kJ/mol, respectively. Because of backbonding, the C–O bond in M\textsubscript{1} is elongated by 2% upon adsorption, leading to a redshift of the calculated CO stretching mode (1994 cm\textsuperscript{-1} for M\textsubscript{1} compared to 2126 cm\textsuperscript{-1} for gas phase CO, which is 18 cm\textsuperscript{-1} lower than the experimental value of 2144 cm\textsuperscript{-1} in ref \textsuperscript{55}). A similarly redshifted CO stretching mode (2005 cm\textsuperscript{-1}) was experimentally observed for CO on Pd/MgO\textsubscript{(001)}.\textsuperscript{22} Upon O\textsubscript{2} adsorption, the O–O bond is elongated by 4%, which corresponds to the formation of a superoxide species. The coadsorption energy (−131 kJ/mol in M\textsubscript{2}) includes a destabilizing interaction of ΔE\textsubscript{dest} = 25 kJ/mol, as both adsorbates compete for electron density from Pt. While the preferred adsorption mode of CO is not affected by varying the support, O\textsubscript{2} was found to preferably adsorb on a bridging site between two surface cations on the reducible oxide supports.

The oxidation barrier via TS\textsubscript{1} (cf. Figure 2) amounts to 38 kJ/mol, which is significantly lower than the value reported in ref \textsuperscript{27} (133 kJ/mol). Li and co-workers\textsuperscript{27} used the same density functional (PBE) and a comparable unit cell size, i.e. p(3 × 3) compared to c(2 × 2) in this work. However, they did not allow for surface relaxation, which stabilizes intermediates and transition state structures significantly. Along the imaginary mode of TS\textsubscript{1} (595 cm\textsuperscript{-1}), the O–O bond breaks, and an O atom is transferred to CO.

CO\textsubscript{2} desorption from the resulting PtO cluster (M\textsubscript{3}) is 153 kJ/mol endothermic (gray path starting with M\textsubscript{3} in Figure 2). Alternatively, a second CO molecule may adsorb atop a Mg\textsuperscript{2+} ion in the vicinity of the active site with an adsorption energy of −18 kJ/mol (M\textsubscript{4}). Adsorption atop the Pt atom is less favorable in the presence of adsorbed CO\textsubscript{2} and atomic O\textsubscript{2}.

The oxidation barrier via TS\textsubscript{2} amounts to 33 kJ/mol, which is lower than the barrier for the first oxidation step (38 kJ/mol). Along the imaginary mode of TS\textsubscript{2} (438 cm\textsuperscript{-1}) the CO molecule moves toward the O atom, and the Pt–O bond is elongated. Starting with M\textsubscript{5}, CO\textsubscript{2} desorption is only mildly endothermic (19 kJ/mol for each CO\textsubscript{2} molecule). Compared to the PtO species M\textsubscript{3}, which binds CO\textsubscript{2} more strongly (153 kJ/mol), the Pt atom of M\textsubscript{5} is 15 pm closer to the MgO(001) surface (see side views in Figure 2). As the Pt species binds more strongly to the Mg\textsuperscript{2+} cations, it binds CO\textsubscript{2} less strongly, facilitating the desorption step after the formation of the second CO\textsubscript{2} molecule.

Calculated adsorption energies and barrier heights for single-atom catalysts studied in this work are compiled in Table 2. On Pt/MgO\textsubscript{(001), intrinsic barriers amount to 45 kJ/mol (Pt/FeO\textsubscript{2}), 36 kJ/mol (Pt/MnO\textsubscript{2}), and 38 kJ/mol (Pt/MgO). Our experimentally determined apparent barriers (Figure S2) are slightly lower than the calculated intrinsic barriers, that is, 15 kJ/mol (Pt/FeO\textsubscript{2}), 28 kJ/mol (Pt/MnO\textsubscript{2}), and 30 kJ/mol (Pt/MgO\textsubscript{2}). This is likely due to the weak binding energies for O\textsubscript{2} in the presence of a preadsorbed CO molecule, which is why the experimental barrier refers to the transition from M\textsubscript{1} to M\textsubscript{3} (Figure 2). The most exothermic O\textsubscript{2} binding energy was calculated for Pt/FeO\textsubscript{2}, which would explain why the apparent oxidation barrier is lower on the FeO\textsubscript{2} support.

On Pd/MgO\textsubscript{(001), the intrinsic CO oxidation barrier amounts to 64 kJ/mol. Using the Redhead equation,\textsuperscript{56} this barrier would correspond to a CO\textsubscript{2} desorption peak at 250 K in temperature-programmed reaction experiments, which is close to the observed peak at 260 K.\textsuperscript{23}

On each metal oxide support, intrinsic oxidation barriers increase in the order Au < Pt < Pd. While Bader charges Q on the metal atoms and adsorption energies of CO and O\textsubscript{2} depend on the nature of the support, CO oxidation barriers are surprisingly similar. On Au and Pt atoms, CO oxidation barriers are within 5 and 9 kJ/mol, respectively, regardless of the support. For Pd atoms, a larger spread (22 kJ/mol) was obtained. However, even this larger spread is still within the accuracy of our DFT approach. Furthermore, each system is predicted to show CO oxidation activity at low temperatures due to the small intrinsic barriers.

To gain a more detailed understanding of the factors contributing to the oxidation barrier ΔE\textsubscript{‡}, the barrier is decomposed into the following terms: (i) ΔE\textsubscript{CO} is the energy

![Figure 2. Energy profile for the CO oxidation on Pt/MgO with cross-sectional views on reaction intermediates. The following color code is used throughout this work: C (black), Mg (green), O (red), and Pt (gray). The axis label M indicates a minimum, whereas TS represents a transition state along the reaction coordinate.](image-url)
required to move an isolated CO molecule from its most stable adsorption site to its position in TS1; (ii) \( \Delta E_{O2} \) is the energy required to move an isolated O\(_2\) molecule from its most stable adsorption site to its position in TS1; and (iii) \( \Delta E_{int} = \Delta E^f - \Delta E_{CO} - \Delta E_{O2} \) is the interaction energy between CO and O\(_2\) in TS1. The energy contributions are compiled in Table S4. The total CO uptake amounts to 1604 \( \mu \text{mol/gcat} \). As CO can bind to other vacancy-type defects (e.g., Schottky-type double vacancies) as well,\(^{58}\) this should be considered an upper limit for the O vacancy concentration.

The infrared signal at 1356 cm\(^{-1}\) is notably absent for CO adsorbed on Pt/MgO, (Figure 4b), which indicates that Pt binds to the O vacancies instead. This interpretation is further supported by a decrease in the amount of weakly adsorbed CO in the titration experiments (0.47 \( \mu \text{mol/gcat} \)).

On Pt/MgO\(_{at}\) additional infrared features are observed at 2039, 1997, 1966, and 1857 cm\(^{-1}\). The peak at 1997 cm\(^{-1}\) is assigned to CO on Pt atoms inside O vacancies (1994 cm\(^{-1}\) from DFT), and the shoulder at 1966 cm\(^{-1}\) is assigned to the symmetric C–O stretching mode of two coadsorbed CO molecules on single Pt atoms inside O vacancies (1978 cm\(^{-1}\) from DFT); the antisymmetric C–O stretching mode (1935 cm\(^{-1}\) from DFT) is predicted to be nearly IR-inactive because of the small dipole change along the normal mode. However, the intensity of the peak at 1997 cm\(^{-1}\) is significantly higher, which indicates that single Pt atoms predominantly bind one CO molecule. The left-hand shoulder at 2039 cm\(^{-1}\) is assigned to CO atop metallic Pt atoms (2045 cm\(^{-1}\) for Pt(001) from DFT), and the peak at 1857 cm\(^{-1}\) is assigned to CO in a bridged configuration on Pt facets (1842 cm\(^{-1}\) for Pt(001) from DFT). For positively charged Pt species, significantly more blue-shifted CO stretching modes have been reported (e.g., 2118 cm\(^{-1}\) for Pt/Al\(_2\)O\(_3\) and 2098 cm\(^{-1}\) for Pt/CoO\(_x\), in refs 8 and 14, respectively), which indicates that no such species are present on the MgO support. Thus, our Pt/MgO\(_{at}\) catalyst contains a mix of O vacancy-supported single atoms and Pt clusters/particles.

To study the oxidation of preadsorbed CO, 10% O\(_2\) in He was introduced into the cell at 296 K. The resulting infrared spectrum (Figure 4c) shows a decrease in the adsorption band intensity for CO adsorbed on Pt/MgO (1997 cm\(^{-1}\)). Compared with CO, O\(_2\) binds less strongly to Pt/MgO\(_{at}\) (−42 kJ/mol for O\(_2\) and −109 kJ/mol for CO), so the loss in infrared intensity is likely a result of CO oxidation rather than displacement of CO by O\(_2\) at this temperature. Furthermore, two additional infrared bands are observed at 2362 and 2339 cm\(^{-1}\) (inset in Figure 4), which are assigned to CO\(_2\) product; based on DFT calculations, the C–O stretching mode for CO\(_2\) on Pt/MgO\(_{at}\) is predicted to occur at 1818 cm\(^{-1}\), which would overlap with the broad peak for bridged CO at 1857 cm\(^{-1}\). The peak for CO in a bridging configuration at 1857 cm\(^{-1}\) is blue-shifted to 1868 cm\(^{-1}\) and decreases in intensity as well. This

3.3. Experimental Infrared Spectra and Chemisorption Studies. CO adsorption on bare MgO\(_x\) (Figure 4a) does not lead to detectable infrared features between 2200 and 1800 cm\(^{-1}\); the peak at 1356 cm\(^{-1}\) is assigned to CO molecules inside O vacancies of MgO based on reference frequencies obtained using DFT (1347 cm\(^{-1}\)). DFT binding energies and harmonic frequencies that are discussed in this section have been compiled in Table S4. The total CO uptake amounts to 0.57 \( \mu \text{mol/gcat} \). As CO can bind to other vacancy-type defects (e.g., Schottky-type double vacancies) as well,\(^{58}\) this should be

![Figure 3](image-url) Inverse correlation between \( \Delta E_{CO} \) and \( \Delta E_{O2} \) (cf. Table 2). The black line refers to the linear fit \( \Delta E_{O2} = 60 \text{ kJ/mol} - \Delta E_{CO} \) (\( R^2 = 0.41 \)), and the gray area indicates an uncertainty of ±10 kJ/mol. The color of the spheres indicates the support material: red (FeO\(_x\)), white (MnO\(_x\)), blue (NiO\(_x\)), and green (MgO\(_x\)).

![Figure 4](image-url) Infrared spectra of (a) MgO\(_x\) and (b) 0.1 Pt/MgO\(_x\) after exposure to 2 kPa CO and purging under flowing He at 296 K. (c) The CO-covered Pt/MgO\(_x\) sample was then exposed to 10% O\(_2\) for 30 min (flow rate 50 mL/min) at 296 K. The inset shows C–O stretching features resulting from CO\(_2\).
Figure 5. (a) Schematic representing the mechanism for catalyst deactivation upon healing the O vacancy and (b) reaction energies for the first deactivation step (ΔE_{relax}) as a function of the O vacancy formation energies (ΔE_{form}) for the single-atom catalysts considered in this work. (c) The experimentally measured onset temperature of Pt sintering is estimated from the maxima of the second order derivatives of the CO oxidation turnover frequencies (eq 6). (d) Sintering-onset temperatures determined from our experiments (panel c) decrease with increasing calculated O vacancy formation energies of the supporting oxide.

indicates that CO oxidation may also occur on the Pt clusters/particles, although less CO is converted there. Furthermore, the H₂ uptake was measured for the Pt/MgO₀.₅ catalyst before and after the temperature-programmed CO oxidation experiments between 303 and 473 K. The H₂ uptake of the freshly prepared catalyst amounts to 0.13 μmol/gcat after the pretreatment. After the temperature-programmed reaction (i.e., after the catalyst was exposed to CO and O₂ at 473 K), the H₂ uptake was below the uncertainty of our chemisorption experiments (<0.01 μmol/gcat). For our 0.1 wt % Pt catalyst, this translates into a H/Pt ratio below 0.002, which is close to the value for extended Pt particles and therefore indicates Pt sintering.

After Pt was deposited on the FeOₓ support, a similar decrease in the amount of free O vacancy sites was observed via CO titration. On bare FeOₓ, the total CO uptake amounts to 1.34 μmol/gcat, which is significantly higher than on MgOₓ, due to the higher binding energy of CO (cf. Table S4). After Pt was added, the amount of weakly adsorbed CO decreased (0.95 μmol/gcat), which indicates that Pt binds to the vacancies again. However, because of the mechanical properties of FeOₓ, we were unable to prepare the pellets needed to perform infrared measurements. The hydrogen uptake of Pt/FeOₓ prior to the temperature-programmed CO oxidation experiments (0.14 μmol/gcat) is similar to the value for Pt/MgOₓ (0.13 μmol/gcat), indicating similar levels of Pt dispersion. After the CO oxidation experiments, the hydrogen uptake of Pt/FeOₓ was lower (0.08 μmol/gcat), but the decrease is significantly smaller than for Pt/MgOₓ, which indicates lower sintering rates.

3.4. Catalyst Deactivation. For most supporting oxides considered in this work, DFT calculations show that the MeO species (M3 in Figure 2) is metastable at the O vacancy, as the migration of the O atom (left behind after O₂ dissociation) into the vacancy (Figure 5a) is highly exothermic. The energy gain upon relaxation (ΔE_{relax}) depends on the O vacancy formation energy of the support, which is shown in Figure 5b for Pt and Pd on the four different supports considered here. For transition metal atoms supported on MgO(001), migration barriers obtained by Xu et al. using DFT are below 80 kJ/mol. Since atomic dispersion is not favorable on the pristine (001) surfaces, metal particle formation (cf. Figure 5a) is predicted to occur readily even at moderate temperatures once the O vacancy is healed.

Temperature-programmed reaction experiments on Pt/FeOₓ, Pt/MgOₓ, and Pt/MnOₓ show different temperature dependencies for CO oxidation rates at low and elevated temperatures. At low temperatures, turnover frequencies increase exponentially with 1/T, but as the temperature increases above a specific support-dependent temperature, the slope becomes steeper (i.e., the activation barrier increases), leading to turnover frequencies similar to metal particles. The Arrhenius plots are shown in Figure S2. This behavior is attributed to catalyst sintering: as the Pt atoms begin to agglomerate, the identity of active site changes, leading to different CO oxidation barriers. Pt sintering was confirmed by H₂ chemisorption experiments as discussed in the previous section.

The onset temperature for Pt sintering was determined from our experiments by locating the inflection point of the CO oxidation rate/temperature activation energy (i.e., the first derivative of ln(TOF) with respect to 1/T), which is calculated using the finite difference approximation

\[
\frac{d[\ln \text{TOF}]}{d[1000K/T]} \approx \frac{[\ln \text{TOF}]_{i+1} - [\ln \text{TOF}]_{i-1}}{[1000K/T]_{i+1} - [1000K/T]_{i-1}}
\]

where TOF denotes turnover frequencies (per total number of Pt atoms) between 303 and 473 K and the subscript i denotes the corresponding indices of the data points. Noise was removed from this data using the moving average method with a period of 15. The second derivative, which has a maximum at the inflection point of eq 6, was then obtained using the same approach.
Figure 5c shows the second-order derivatives of the rates, which have maxima at 336 K for Pt/MgO, 348 K for Pt/MnO, and 363 K for Pt/FeO. For Pt/MgO, Landmann and co-workers observed sintering around 300 K, which indicates that single Pd atoms are less stable than Pt atoms on O-defective MgO. This is in good agreement with our predictions that single Pd atoms are less stable than Pt atoms on O-vacant supports.23 In summary, the reducibility of the support is an important parameter for the stability of anionic single-atom catalysts. High O vacancy formation energies lead to strong binding of Pd and Pt atoms inside the vacancy, but the O vacancies heal quickly in an oxidizing environment, which leads to catalyst deactivation. On the other hand, support materials with low O vacancy formation energies bind Pd and Pt atoms less strongly. Therefore, metal oxides with intermediate O vacancy formation energies such as FeO and MnO are the most desirable support materials because they are able to stabilize transition metal atoms inside O vacancies that heal slowly in an oxidizing environment. Since CO oxidation barriers depend primarily on the identity of the transition metal atom (Table 2), changing the support does not affect the activity significantly.

4. CONCLUSIONS

On the basis of DFT calculations, we predict that Pd and Pt can form stable single-atom catalysts inside the O vacancies of MeO (Me = Fe, Mg, Mn, and Ni); for Pt/MgO, the presence of such species was confirmed using infrared spectroscopy. Metal atom binding energies inside the O vacancies depend on the vacancy formation energies of the supporting metal oxide and the lattice match between transition metal and support. Due to charge transfer into the metal d states, these systems can activate dioxygen at low temperatures by forming superoxide species; intrinsic barriers were found to depend primarily on the identity of the transition metal. On supporting metal oxides with O vacancy formation energies larger than FeO(001), the CO oxidation pathway involves a metastable metal monoxide species that can heal the O vacancy, leading to metal sintering and thus catalyst deactivation between 300 and 400 K. Therefore, the O vacancy formation energy of the support is an important parameter for the stability of anionic single-atom catalysts, while their activity depends primarily on the identity of the transition metal atom.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b03298.

Bulk metals; binding energies of transition metal atoms; descriptor for metal binding energies; binding energies and vibrational frequencies for adsorbed CO; barrier decomposition; Arrhenius plots and infrared spectra after CO oxidation; and structure files (PDF).

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Notes

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