Revealing the catalytic kinetics and dynamics of individual Pt atoms at the single-molecule level

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Due to the importance of single-atom catalysts (SACs), here, the catalysis of Pt SAC was studied at the single-molecule single-atom level. Both static and dynamic activity heterogeneity are observed in Pt SAC. It reveals that the intrinsic catalytic activity of Pt SAC is higher than that of Pt nanoparticles (NPs), although they follow the same bimolecular competition mechanism. Significantly, Pt SAC presents no catalysis-induced surface restructuring, meaning that the dynamic activity fluctuation of Pt SAC can only be attributed to the spontaneous surface restructuring, and the catalysis process does not affect much of the structure of Pt1-based active sites, all different from Pt NP catalysis, in which the surface restructuring and the catalysis can affect each other. Further, density functional theory (DFT) calculation indicates that the unique catalytic properties of Pt SAC or the different catalytic properties between Pt SAC and NPs could be attributed to the strong adsorptions of both reactant and product on Pt SAC, large surface energy of Pt SAC, and strong binding of Pt1 on support. Knowledge revealed here provides fundamental insights into the catalysis of atomically dispersed catalyst.

Atmospheric dispersed metals or metal single-atom catalysts (SACs) have recently attracted a large amount of attention due to their extremely high atom efficiency or metal utilization (~100%) (1–4). For precious metals, such as Pt (3, 5, 6), Au (7, 8), Pd (9–11), and Ir (12, 13), their SACs as the most cost-effective catalysts are very desirable for practical applications.

For metal SACs, the individual metal atoms are anchored tightly on supports (such as carbon materials, metals, or metal oxides) via a strong interaction between individual metal atoms and supports (6, 10, 14, 15). Such strong anchoring usually occurs via the vacancy or defects on supports (5, 11, 13, 16). The catalytic activity or selectivity of a SAC usually depends strongly on the choice of support (3, 17–21), which directly determines the structure of the single-metal atom–based active sites. To deeply understand the unique catalytic properties of SACs and reveal the property differences between traditional metal nanoparticle (NP)-based catalysts and SAC (6, 9, 13, 15, 22–24), here, based on single-molecule fluorescence microscopy (SMFM) (25–29), we study the nanocatalysis of Ceria (CeO2)-supported (30) Pt SAC for a fluoregenic reaction (31, 32) at the single-molecule single-atoms level in real time with single-turnover resolution. It reveals both static and dynamic activity heterogeneity in the catalysis of Pt SAC. Significantly, no catalysis-induced surface restructuring can be observed on Pt SAC, which means that the dynamic activity fluctuation of Pt SAC can only be attributed to the spontaneous surface restructuring, and the catalysis process does not affect the surface restructuring of Pt SAC on CeO2. Further, density functional theory (DFT) calculation indicates that the observed unique catalytic properties of Pt SAC and the difference of catalytic properties between Pt SAC and NPs could be attributed to the stronger adsorptions of both reactant and product on Pt SAC, larger surface energy of Pt SAC, and stronger binding of Pt1 on CeO2 than those on Pt NPs. Such results deepen our understanding of the intrinsic catalytic properties of SAC and may help in the design of highly efficient SACs.

Results and Discussion

Synthesis and Characterization of Atomically Dispersed Pt1@CeO2. CeO2 nanocrystals, the support of Pt SACs adopted here, were synthesized based on literature (33), with Ce(NO3)3 as precursor via hydrothermal treatment at 160 °C and then pyrolysis at 1,000 °C sequentially. As shown in Fig. 1 A and B, the obtained CeO2 nanocrystals with an average size of about 112 ± 6 nm could be dispersed individually without aggregation. After the sparse deposition of individual Pt atoms on CeO2 nanocrystals, the catalytic kinetic and dynamical properties of Pt1@CeO2 were studied using single-molecule fluorescence microscopy (SMFM).

Significance

Here, with single-molecule fluorescence microscopy, we study the catalytic behavior of individual Pt atoms at single-turnover resolution, and then reveal the unique catalytic properties of Pt single-atoms catalyst and the difference in catalytic properties between individual Pt atoms and Pt nanoparticles. Further density functional theory calculation indicates that unique catalytic properties of Pt single-atoms catalyst could be attributed intrinsically to the unique surface properties of Pt1-based active sites.
(SI Appendix), the obtained sample, named as Pt₀.₀₅CeO₂, was characterized by high-angle annular dark-field scanning transmission electron micros (HAADF-STEM) to monitor the dispersion of individual Pt atoms on CeO₂ support. Typically, for the sample of Pt₀.₀₅CeO₂ with Pt loading of 0.05 wt.% (Fig. 1C), as expected, the individual Pt atoms are dispersed sparsely on the surface of CeO₂ nanocrystals. To study the catalytic activity of Pt₀.₀₅CeO₂, the Pt-catalyzed fluorogenic reaction (the reduction reaction of nonfluorescent resazurin to highly fluorescent resorufin by H₂; Fig. 1D) was adopted as the model reaction (31, 32). The control experiment shows that the pure CeO₂ nanocrystals are inert to such reaction (SI Appendix, Fig. S1); only with the addition of Pt₀.₀₅CeO₂, the reduction reaction of resazurin by hydrogen can occur rapidly as indicated by the time-dependent increase of fluorescence signal of the product resorufin at 583 nm (Fig. 1D and SI Appendix, Fig. S1), confirming that the individual Pt atoms (Pt₀.₀₅CeO₂) just like traditional Pt NPs (31), indeed, can effectively catalyze such fluorogenic reduction reaction.

The single-molecule nanocatalysis of Pt₀.₀₅CeO₂ was then done based on the above fluorogenic reaction. To study the nanocatalysis of such Pt SAC at the single-molecule single-atom level, based on the mass density (1.9 g/mL) of obtained powder of CeO₂ nanocrystals with an average size of 112 nm (Fig. 1A and B), a Pt₀.₀₅CeO₂ catalyst with an extremely low Pt loading of 0.00001 wt.% (or 0.1 ppm) (SI Appendix, Scheme S1) was synthesized for the fluorogenic reaction to make sure that the averaged number (n) of Pt atoms on a single CeO₂ NP is much smaller than one (n < 1). It means, for such Pt₀.₀₅CeO₂, there is statistically only one or zero Pt atoms on the surface of a single CeO₂ nanocrystal. By sparsely dispersing such individual CeO₂ NPs with one or zero Pt atoms on a quartz slide surface (SI Appendix, Fig. S2), one can make sure that the fluorescence signal obtained from each location is from the product molecules formed on a single Pt atom sitting on a CeO₂ nanocrystal (Fig. 2A). Such single-molecule nanocatalysis was conducted in a microfluidic channel, as shown in Fig. 2B. By flowing the solution containing both nonfluorescent resazurin and saturated hydrogen into the channel, the reduction of resazurin by hydrogen was then catalyzed by Pt₀.₀₅CeO₂ to produce rapidly fluorescent product resorufin, which was then excited by a green (532 nm) laser to produce fluorescence and detected via an electron-multiplying charge coupled device (EMCCD) camera at an operating rate of 100 ms per frame. The stochastic fluorescence bursts at many localized spots with individual Pt₀.₀₅CeO₂ were recorded in movies by total internal reflection fluorescence (TIRF) microscope (34, 35); each spot gives out a stochastic trajectory with fluorescence bursts (Fig. 2C) to indicate the in situ catalysis process occurring on a single Pt atom–based active site (26). Each fluorescence burst could be attributed to the formation and the subsequent dissociation of a fluorescent product resorufin molecule on a single Pt atom–based active site. The observed stochastic fluorescence off-on signal on turnover trajectory of fluorescence contains two waiting times, τₐ₇ and τₐ₈ (Fig. 2C), by dividing a catalytic cycle into two parts. τₐ₇ is the waiting time before the formation of a product molecule; τₐ₈ represents the time that one product molecule spends before it dissociates from catalyst surface (26).

The Catalytic Kinetics of Atomically Dispersed Pt₀.₀₅CeO₂. It has been known that the above τₐ₇ contains the kinetic information of the catalytic product formation process, and τₐ₈ contains that of product dissociation process (26). Therefore, the whole catalytic kinetics on a single Pt atom can be probed by resolving these two waiting times. Here, the reaction kinetics can be defined by the statistical properties. The statistical properties of <τₐ₇>⁻¹ and <τₐ₈>⁻¹ obtained from a single trajectory represent the time-averaged product formation rate and product desorption rate on a Pt atom, respectively (26). When averaging the turnover trajectories from many individual Pt atoms, the relationship between reaction rate and substrate concentrations can be obtained reliably. Interestingly, as shown in Fig. 3A, in the H₂-saturated ([H₂] = 0.8 mM) solution, the average product formation rate (<τₐ₇>⁻¹) on a single Pt atom initially increases with substrate resazurin concentration and then decreases inversely after a maximum, similar to the catalytic product formation process on a single Pt NP for the same reaction (SI Appendix, Fig. S3A) (31). Obviously, such decay of the product formation rate at high substrate concentration could be attributed to the bimolecular competition mechanism between two different substrate molecules (resazurin and hydrogen) (25, 29) rather than the deactivation (SI Appendix, Fig. S4). Moreover, as shown in SI Appendix, Fig. S5, at the same substrate concentration and reaction temperature (298 K), the product formation rates obtained here on a single Pt atom (Pt₀.₀₅CeO₂) are all smaller than that on a single Pt NP with an average size of 4.9 nm (31), mainly due to the fact that the product formation rate on a single Pt NP is the sum of the product formation rates of multiple Pt active sites on the surface of a Pt NP. As for the product desorption process on a single Pt₀.₀₅CeO₂, Fig. 3B shows that the product dissociation rate (<τₐ₈>⁻¹) is independent of the substrate concentration, which is also the same as that observed from traditional single Pt NP for the same product dissociation process (SI Appendix, Fig. S3B) (31).

The above analysis indicates that the total catalytic reaction follows the bimolecular reaction mechanism (25, 29), as shown in Fig. 3C, in which the substrate and product molecules maintain fast adsorption/desorption equilibrium on the catalyst.
Based on previous knowledge, the product formation rate per particle can be expressed as (26)\[
\langle \tau_{\text{off}} \rangle^{-1} = \frac{A_0 A_I}{\tau_1 A_I + \tau_2 + \frac{G[A]}{1 + G[B]}},
\]
and the product dissociation rate is\[
\langle \tau_{\text{on}} \rangle^{-1} = \frac{\tau_2 G[B] + \tau_3}{1 + G[B]}.\]

Here, $[A]$ and $[B]$ represent the concentrations of H$_2$ and resazurin, respectively; $\gamma_{\text{eff}} = \gamma_{\text{eff}}(n_T)$ is the effective rate constant for the catalytic product formation process on a single particle (Fig. 3A); $\gamma$ is the effective rate constant per active site; $n_T$ is the total number of active site on a single particle; $A_i$ and $B_i$ are the adsorption equilibrium constants of H$_2$ and resazurin; $\gamma_2$ and $\gamma_3$ are the rate constants for the indirect and direct dissociation process of product; and $G = (\gamma_1[A]/(\gamma_1 + \gamma_3))$. For this case, since there is only one or zero atom on a single CeO$_2$ NP (Pt$_1$@CeO$_2$), then, $n_T=1$, so $\gamma_{\text{eff}} = \gamma$.

By fitting the experimental data of the product formation rates and dissociation rates using the above equations (Fig. 3A and B), the corresponding kinetic parameters for the product formation process ($\gamma_{\text{on}}$, $\gamma_{\text{off}}$, and $\gamma_{\text{eff}}$) and product direct dissociation process ($\gamma_3$) were obtained as shown in Table 1. To reveal the difference of the catalytic properties between single Pt atoms and single Pt NPs, the kinetic parameters obtained before for single Pt NPs ($\sim 4.9$ nm) (31) for the same reduction reaction are also listed in Table 1 for comparison. It clearly shows that the effective rate constant $\gamma_{\text{eff}}$ per Pt NO is about 4 times that per Pt atom obtained here, mainly due to the fact that the number of active sites ($n_T$) on a single Pt NP is much larger than one (Table 1). While, due to the fact that the value of $n_T$ on a single Pt NP ($\sim 4.9$ nm) is much larger than one or five, one can expect that the value of “apparent” $\gamma = \gamma_{\text{eff}}/n_T$ per active site on Pt NP is smaller than that per active site on Pt SAC (Pt$_1$@CeO$_2$), such a difference could be mainly attributed to the different structure of active sites and the steric hindrance effect induced by the crowding of active sites on the surface of traditional Pt NPs (SI Appendix, Fig. S6); it is also part of the reason for the higher atom efficiency or metal utilization of SAC than traditional metal NPs. As for the adsorption ability of substrate molecules, as shown in Table 1, H$_2$ adsorption on Pt$_1$@CeO$_2$ is stronger than that on Pt NPs, while the resazurin adsorption on Pt$_1$@CeO$_2$ shows no big difference from that on Pt NPs; as for the desorption of product resorufln, $\gamma_3$ in Table 1 shows that the direct dissociation pathway on Pt NPs is faster than that on Pt$_1$@CeO$_2$, indicating that the adsorption of product resorufln on Pt$_1$@CeO$_2$ is stronger than that on Pt NPs.

**The Static Heterogeneity of Catalytic Activity of Atomically Dispersed Pt$_1$@CeO$_2$.** In order to further quantify the difference of catalytic activity of individual atomically dispersed Pt$_1$@CeO$_2$, the probability density function $f_{\text{eff}}(\tau)$ (26, 36) of $\tau_{\text{eff}}$ for product formation process was adopted to evaluate the static heterogeneity of the catalytic activity among different single Pt atoms,

$$f_{\text{eff}}(\tau) = \gamma_{\text{app}} \exp(-\gamma_{\text{app}} \tau).$$

Here, $\gamma_{\text{app}}$ is the apparent catalytic rate constant for product formation process on a single Pt atom (Pt$_1$@CeO$_2$). As shown in Fig. 3D, a typical distribution of $\tau_{\text{eff}}$ from one turnover trajectory was fitted with Eq. 3 to obtain the value of apparent catalytic rate constant $\gamma_{\text{app}}$ of a single Pt atom on CeO$_2$. Fig. 3E shows the distribution of $\gamma_{\text{app}}$ from multiple individual Pt atoms. The broad distribution of $\gamma_{\text{app}}$ corresponding to a large value (90%) of the heterogeneity index (defined as the full width at half maximum/ln4)$^{1/2}$ [full width at half maximum from the Gaussian distribution] divided by the average $\langle \gamma_{\text{app}} \rangle$) (31), indicates a huge static activity heterogeneity among different individual Pt atoms. Such static heterogeneity...
could be attributed to the different microenvironments among different individual Pt atoms mainly induced by the support of CeO₂ nanocrystals, such as the different facets with different oxygen vacancies or defects for the anchoring of individual Pt atoms (37–39).

The Catalytic Dynamics of Atomically Dispersed Pt₁@CeO₂. To further study the catalytic dynamics of individual atomically dispersed Pt₁@CeO₂, we determined the activity fluctuations of multiple individual atomically dispersed Pt₁@CeO₂. The activity fluctuations are reflected by the variation of reaction rates in both the product formation process (τ₁,off) and product dissociation process (τ₁,off). Here, to analyze the activity fluctuations of individual Pt atoms on CeO₂, the individual τ₁,off and τ₁,off were extracted from multiple individual turnover trajectories, and then calculated with the autocorrelation function C₉(m) = ⟨Δτ(0)Δτ(m)/Δτ²⟩ (26). Here, τ represents τ₁,off or τ₁,off and m is the turnover index number from the sequence, and Δτ(τ) = τ(m) − ⟨τ⟩. If Pt₁@CeO₂ possesses catalytic dynamic heterogeneity, C₉(m) will be positive and show a decay behavior with a decay time constant; such a time constant is the activity fluctuation correlation time (26).

As shown in Fig. 4 A and B, both the typical C₉(τ₁,off) and C₉(τ₁,off) present an exponential decay trend, indicating the existence of activity fluctuations in the catalytic product formation (τ₁,off) and dissociation (τ₁,off), respectively, occurring on the active sites of single Pt₁@CeO₂. For the single-atom Pt corresponding to the data shown in Fig. 4 A and B, the decay constants of C₉ at a certain substrate concentration are m₁,off = 1.9 ± 0.5 turnovers and m₁,off = 1.2 ± 0.4 turnovers. Based on the average turnover time (83 s) of this turnover trajectory, the fluctuation correlation times for the τ₁,off and τ₁,off reactions are ~159 and 96 s, respectively. Here, the fluctuation timescales of the dynamic surface restructuring can be reflected by these two correlation times (26). Moreover, the activity fluctuations could be attributed to the small-scale dynamic conformational distortion or distortion. That is to say that the correlation times of fluctuation activity are the timescales of the surface restructuring dynamics. For an SAC of Pt₁@CeO₂, the activity fluctuation of individual atomically dispersed Pt₁@CeO₂ could be attributed to small-scale dynamic conformational restructuring or distortion around the individual active sites, similar to that of NPs (26, 27). Here, the distributions (Fig. 4 A and B, Insets) of the fluctuation correlation times of atomically dispersed Pt₁@CeO₂ are wide (the width of the data distribution is about 200 s), probably due to the different microenvironment around each Pt₁@CeO₂, resulting in the diverse interaction between Pt atoms and support CeO₂.

To further reveal the relevance between activity fluctuations and surface restructuring, we plotted the activity fluctuation rates (ν₁,off = ν₁,off + ν₁,cat-off, ν₁,off = ν₁,cat-on + ν₁,cat-on) against the turnover rates at various reactant concentrations for both the τ₁,off and τ₁,off processes (26). Here, the fluctuation rates are the inverses of the correlation times. As shown in Fig. 4 C, for atomically dispersed Pt₁@CeO₂, the activity fluctuation rates for both the τ₁,off reaction and the τ₁,off reaction are

| Table 1. Comparison of the catalytic kinetics and dynamics between Pt SAC and Pt NPs (31) |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| n_ν | ν₁,off (s<sup>−1</sup>) | ν₁,off (s<sup>−1</sup>) | ν₁,cat-on (mM<sup>−1</sup>) | ν₁,cat-off (mM<sup>−1</sup>) | ν₁,cat-on (s<sup>−1</sup>) | ν₁,cat-off (s<sup>−1</sup>) |
| Pt NPs | >1 | 0.51 ± 0.12 | (0.51/n_ν) | 0.31 ± 0.20 | 0.28 ± 0.15 | 2.35 ± 0.02 | 0.003 ± 0.001 | 0.002 ± 0.001 |
| Pt₁@CeO₂ | 1 | 0.12 ± 0.02 | 0.12 | 1.07 ± 0.10 | 0.32 ± 0.05 | 1.91 ± 0.10 | 0.007 ± 0.001 | 0.011 ± 0.002 |
almost independent of the turnover rates (Fig. 4C), indicating that the fluctuation rate does not change with the substrate concentration, and the values of both \( \tau_{\text{data-off}} \) and \( \tau_{\text{data-on}} \) are zero at any substrate concentration. The substrate concentration–independent activity fluctuation observed here on Pt SAC reflects that the underlying dynamic conformation restructuring existing among atomically dispersed Pt\(_1\)@CeO\(_2\) is mainly due to the spontaneous surface restructuring of the single-atom Pt–based active site (Pt\(_1\)@CeO\(_2\)) (26); the catalytic process or the substrate binding/product unbinding approximately has no effect on structure of the Pt SAC-based active sites. As for the Pt NPs, interestingly, as shown in SI Appendix, Fig. S7 and reported before (31), the catalytic process or the substrate binding/product unbinding can affect hugely the surface restructuring of the Pt NP surface, which is also called “catalysis-induced surface restructuring.” Such a huge difference between Pt SAC and the Pt NPs revealed here probably indicates that the binding of Pt\(_1\) to CeO\(_2\) is much stronger than the binding of Pt\(_1\) to Pt\(_{\text{NP}}\), or the structure of Pt\(_1\)-CeO\(_2\) is much more stable than that of Pt\(_1\)-Pt\(_{\text{NP}}\). Furthermore, as shown in Fig. 4C and Table 1, the rate of spontaneous surface restructuring can be obtained (\( \tau_{\text{open-off}}=0.007 \pm 0.001 \) s\(^{-1}\) for the product formation process \( \tau_{\text{off}} \) and \( \tau_{\text{on}}=0.011 \pm 0.002 \) s\(^{-1}\) for product desorption \( \tau_{\text{prod}} \) process), corresponding to a timescale of about 90 s to 160 s of the spontaneous surface reconstruction. The revealing of two different rates of spontaneous surface restructuring indicates that there are at least two different models of spontaneous surface restructuring on the same surface; the slow one (0.007 \( \pm \) 0.001 s\(^{-1}\)) can affect the product formation process or the substrate binding, and the faster one (0.011 \( \pm \) 0.002 s\(^{-1}\)) can affect the product dissociation process or the product unbinding. Interestingly, as shown in Table 1, for both the product formation and dissociation process on Pt NPs, the rates of spontaneous surface restructuring are smaller than that on Pt SAC (Pt\(_1\)@CeO\(_2\)), indicating that the structure of the individual Pt active site on Pt NP is much more stable than that of the single Pt atom–based active site on CeO\(_2\) surface, and the reactant binding/product unbinding can activate the surface of Pt NPs and speed up or enhance its surface restructuring.

Furthermore, we did a DFT calculation to deeply understand the above observation about the unique properties of Pt SAC and the property differences between Pt SAC and Pt NPs(Pt\(_{\text{NP}}\)) shown above in Table 1. Based on the HAADF-STEM image (Fig. 1C) of Pt\(_1\)@CeO\(_2\) and previous reports about the structure of Pt\(_1\)@CeO\(_2\) (33, 38), DFT calculations about Pt\(_1\)@CeO\(_2\) were done here based on a model with individual Pt atoms trapped by surface Ce vacancies on CeO\(_2\) crystals (Fig. 5 and SI Appendix, Table S1). Firstly, we calculated the adsorption energies (E\(_{\text{ad}}\)) of both reactants and products on different surfaces. For the case with the coexistence of one H\(_2\) molecule and one resazurin molecule around the active site (SI Appendix, Fig. S8A) (40), results in Fig. 5 show clearly that adsorption energies (E\(_{\text{ad}}\)) of both H\(_2\) (E\(_{\text{ad}}\)\(_{\text{H}_2}\))\(_\text{H}_2\) = \(-0.517\) eV) and resazurin (E\(_{\text{ad}}\)\(_\text{H}_2\)\(_\text{resoru}\) = \(-0.382\) eV) on Pt\(_1\)@CeO\(_2\) are larger than those (E\(_{\text{ad}}\)\(_\text{H}_2\)\(_\text{H}_2\) = \(-0.420\) eV; E\(_{\text{ad}}\)\(_\text{H}_2\)\(_\text{resoru}\) = \(-0.314\) eV) on Pt\(_{\text{NP}}\), indicating stronger adsorptions of both H\(_2\) and resazurin on Pt\(_1\)@CeO\(_2\) than on Pt\(_{\text{NP}}\), consistent with the obtained values of \( \alpha_\text{H}_2\) and \( \alpha'_\text{H}_2\) shown in Table 1. As for the adsorption of product resorufin, its E\(_{\text{ad}}\) on Pt\(_1\)@CeO\(_2\) (\(-0.228\) eV) is also larger than that (\(-0.204\) eV) on Pt\(_{\text{NP}}\), indicating a stronger adsorption of resorufin on Pt\(_1\)@CeO\(_2\) than on Pt\(_{\text{NP}}\), further confirming the slower dissociation (smaller \( \gamma_\text{resoru}\) of product resorufin from Pt\(_1\)@CeO\(_2\) than that from Pt\(_{\text{NP}}\) shown in Table 1. To understand the bimolecular competition mechanism for this redox reaction catalyzed by both Pt\(_1\)@CeO\(_2\) and Pt NPs (Fig. 3C and SI Appendix, Fig. S5), we further calculated E\(_{\text{ad}}\) of reactants (H\(_2\) and resazurin) by increasing the number of H\(_2\) molecules or [H\(_2\)] around the active sites (41, 42). For the case with the coexistence of four H\(_2\) molecules and one resazurin molecule around the active site (SI Appendix, Fig. S8B), Fig. 5 shows the variations of E\(_{\text{ad}}\) with the increase of [H\(_2\)]. For the adsorption on Pt\(_1\)@CeO\(_2\), the adsorption energy of H\(_2\) increases about 17%, while the adsorption energy of resazurin decreases 15% inversely; as for the adsorption on Pt NPs, the adsorption energy of H\(_2\) decreases 57%, while the adsorption energy of resazurin increases inversely about 50%. Obviously, all these results confirm the
bimolecular competition mechanism observed on both Pt$_1$@CeO$_2$ and Pt NPs.

Moreover, we also found that the surface energy ($E_{\text{surf}}$) of Pt$_1$@CeO$_2$ (0.190 eV/Å$^2$) in $SI$ Appendix is larger than that (0.090 eV/Å$^2$) of Pt$_n$, confirming the observed higher activity ($\gamma$) and faster spontaneous surface restructurings ($\nu_{\text{on-off}}$ and $\nu_{\text{on-on}}$) of Pt$_1$@CeO$_2$ than that of Pt NPs (Table 1) (43). Further results (Table 2) show that the binding of a Pt single atom on substrate CeO$_2$ ($E_b = -12.560$ eV) is much stronger than that ($E_b = -6.972$ eV) on Pt NPs, explaining the above observations on Pt$_1$@CeO$_2$ without catalysis-induced surface restructururing (Fig. 4C) and the observations on Pt NPs with catalysis-induced surface restructururing ($SI$ Appendix, Fig. S7) (31). To further confirm such difference, HAADF-STEM was adopted to analyze the possible effect of the catalysis process on the microstructure of the active sites on both Pt$_1$@CeO$_2$ and Pt NPs. As shown in $SI$ Appendix, Fig. S9 A and B, after a long-term (10 h) catalytic process for the fluorogenic reaction shown in Fig. 1 D, the microstructures of Pt$_1$-based active sites on CeO$_2$ show almost no variation; such a fact indicates that the restructuring during catalysis is too gentle to much affect the structure of a Pt$_1$-based active site on CeO$_2$, confirming that the underlying dynamic conformation restructuring existing among atomically dispersed Pt$_1$@CeO$_2$ is mainly due to the spontaneous surface restructuring of the single-atom Pt$_1$-based active site (Pt$_1$@CeO$_2$), while the surface structure of traditional Pt NPs shows tremendous variation after the same catalytic process as shown in $SI$ Appendix, Fig. S9 C and D, indicating that the catalysis process on Pt NPs is relatively violent and then leads to serious surface restructuring. Such facts confirm the above catalytic property differences between Pt$_1$@CeO$_2$ and Pt NPs. Significantly, the stronger binding (large $E_b$) of the Pt atom on CeO$_2$ and the faster spontaneous restructururing of Pt$_1$@CeO$_2$ than Pt NPs indicate that the spontaneous surface restructururing observed on Pt$_1$@CeO$_2$ mainly originates from the surface restructururing of CeO$_2$ around the Pt$_1$ center; it also implies that the reactants/products adsorption/desorption or catalysis process can intensify the restructururing amplitude of a surface with a slow spontaneous restructuring, while, if the initial spontaneous restructuring of a surface is fast enough, then the reactants/products adsorption/desorption or catalysis process cannot much affect its surface restructururing. So, as shown in Table 2, for Pt NPs, the catalytic process and surface restructururing can affect each other, like the previous observation on Au NPs (26), while, for the unique SAC Pt$_1$/CeO$_2$ studied here, its surface restructurering can affect the catalytic process; inversely, the catalytic process cannot affect its surface restructurering. In other words, the fast spontaneous restructurering of a surface can weaken the effect from its environment.

### Table 2. Comparison of surface energy ($E_{\text{surf}}$), binding energy ($E_b$), and effect of the surface reconstruction on catalysis between Pt NPs and Pt$_1$@CeO$_2$

|           | $E_{\text{surf}}$ (eV/Å$^2$) | $E_b$ (eV) | Effect between catalytic process and surface reconstruction of different surfaces |
|-----------|-------------------------------|------------|----------------------------------------------------------------------------------|
| Pt NPs    | 0.09                          | -6.972     | Catalytic process $\rightarrow$ surface reconstruction                             |
| Pt$_1$@CeO$_2$ | 0.19                        | -12.560    | Catalytic process $\rightarrow$ surface reconstruction                             |

### Discussion

In summary, the catalytic behavior of Pt SAC on CeO$_2$ (Pt$_1$@CeO$_2$) was studied via SMFM at the single-molecule single-atomal level. Both static and dynamic activity heterogeneity were observed in the catalysis of Pt$_1$@CeO$_2$. It was found that Pt SAC follows the same bimolecular competition mechanism as Pt NP does for the same catalytic reaction, while the intrinsic catalytic activity per active site on Pt SAC is much higher than that on Pt NPs. Significantly, it was also found that the dynamic activity fluctuation of Pt SAC can only be attributed to the spontaneous surface restructuring, and no catalysis-induced surface restructururing can be observed due to the fast spontaneous surface restructuring, indicating that the catalysis process does not much affect the surface restructururing around the Pt$_1$-based active site on CeO$_2$, different from Pt NP catalysis in which the surface restructurering and the catalysis can affect each other. Further DFT calculation indicates that all these unique catalytic properties of Pt SAC or the difference from Pt NPs could be attributed to the stronger adsorption of both reactant and product on Pt$_1$@CeO$_2$, larger surface energy of Pt$_1$@CeO$_2$, and stronger binding of Pt$_1$ on CeO$_2$ than those on Pt NPs. The knowledge revealed here provides fundamental insights into the catalytic behaviors of atomically dispersed catalyst.

### Experimental Section

#### Materials and Methods.

Platinum(IV) chloride, Cerium(III) nitrate hexahydrate, Propionic acid, and Ethylene glycol. These chemicals were used as received without further purification. Ultrapure Millipore water (18.2 MΩ cm) was used as the solvent throughout. Reactant resazurin was purchased from Sigma-Aldrich.

**Synthesis of single-atom Pt$_1$/CeO$_2$ catalyst.** The synthesis of SAC Pt$_1$/CeO$_2$ with different amount of Pt loading was based on literature (33), with Ce(NO$_3$)$_3$ and PtCl$_4$ as precursors via sequential hydrothermal treatment at 160 °C and pyrolysis at 1,000 °C. The specific reaction process is introduced in $SI$ Appendix. **Single-molecule experiments.** Single-molecule fluorescence measurements were performed on a home-built prism-type TIRF microscope based on an Olympus IX71 inverted microscope ($SI$ Appendix). A continuous wave circularly polarized 532-nm laser beam was focused onto a small region on the sample. Then the fluorescence signal of the product was collected by a water immersion objective, and projected onto a camera controlled by Andor IQ software. The home-written interactive data language program was used to analyze the movies, which allows us to extract a time trajectory of fluorescence intensity from individual fluorescence spots on the sample.

### Data Availability.

All study data are included in the article and/or $SI$ Appendix.

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