

CHEMISTRY

High-loading single Pt atom sites [Pt-O(OH)_x] catalyze the CO PROX reaction with high activity and selectivity at mild conditions

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The preferential oxidation of CO (PROX) in hydrogen-rich fuel gas streams is an attractive option to remove CO while effectively conserving energy and H₂. However, high CO conversion with concomitant high selectivity to CO₂ but not H₂O is challenging. Here, we report the synthesis of high-loading single Pt atom (2.0 weight %) catalysts with oxygen-bonded alkaline ions that stabilize the cationic Pt. The synthesis is performed in aqueous solution and achieves high Pt atom loadings in a single-step incipient wetness impregnation of alumina or silica. Promisingly, these catalysts have high CO PROX selectivity even at high CO conversion (~99.8% conversion, 70% selectivity at 110°C) and good stability under reaction conditions. These findings pave the way for the design of highly efficient single-atom catalysts, elucidate the role of –OH species in CO oxidation, and confirm the absence of a support effect for our case.

INTRODUCTION

An ever-increasing demand for energy and chemicals has triggered a renewed interest in developing highly efficient catalysts and associated processes. H₂ is widely used in the chemical industry and has huge potential in the clean energy field; however, there is usually around 1% CO in the H₂ stream produced by a combination of methane steam reforming and water-gas shift (WGS) reaction processes. It is crucial to provide high-purity H₂ with little or no CO for many chemical processes, such as proton-exchange membrane fuel cells (PEMFCs), ammonia synthesis, and hydrogenation reactions, because the catalysts could be deactivated by trace amounts of CO. Methanation (CO + 3H₂ → CH₄ + H₂O) can be used to remove small amounts of CO (~1%), but the loss of H₂ can be as high as 15% because of the unselective methanation reaction of CO₂ (CO₂ + 4H₂ → CH₄ + 2H₂O) in the reformat (1). This translates to the release of 15 million tons of CO₂ annually, equivalent to 35 million barrels of oil (2), because the production of H₂ is energy-intensive, and the 15% loss is roughly equal to 1.2 million tons of H₂ per year in the United States. Preferential oxidation of CO (CO PROX) is an attractive alternative to purify H₂ (2CO + O₂ + H₂ → 2CO₂ + H₂) and offers a significant reduction in energy loss during the CO removal process. The primary goal of eliminating CO is to meet the stringent requirements of PEMFCs, which require CO levels below 50 parts per million (3). It is challenging for typical catalysts to achieve 50% O₂ selectivity (to CO₂) with complete CO conversion because of the competitive oxidation of H₂ (3).

Noble metals supported on reducible oxide supports are usually highly active for CO oxidation at low temperature and are thus good candidates for CO PROX (4), but debate on the mechanistic role of

the support in CO oxidation is still ongoing. Oh and Sinkevitch (5) reported that Pt, Rh, and Ru are the best CO PROX catalysts among Pt, Pd, Rh, Ru, and base metals (Co/Cu, Ni/Co/Fe, Ag, Cr, Fe, and Mn) with Al₂O₃ as the support. However, it is also widely known that CO is strongly adsorbed on metallic Pt surfaces (6, 7), leading to poor CO oxidation activity at low temperature due to limited accessible sites for O₂. This problem can be overcome by introducing another metal to form bimetallic catalysts with Pt modified to improve CO oxidation catalytic performance (8–11). Flytzani-Stephanopoulos, Sykes, and co-workers (12) have developed a method to successfully anchor single Pt atoms in metallic Cu matrices (called single-atom alloys), changing the electronic properties of the isolated Pt atoms, which greatly reduces CO poisoning because of the weaker interaction between CO and Pt atoms.

It has been reported that the active sites for low-temperature WGS reactions are nonmetallic Pt and Au (13), which were later proven to be single Pt and Au atoms (14–16). These findings focused on the study of atomically dispersed cationic Pt species because of their 100% metal atom utilization efficiency and unique catalytic properties. The single Pt atoms were shown to have weaker CO binding compared to conventional Pt nanoparticle (NP) catalysts, which makes single-Pt atom catalysts more accessible to O₂, which can lead to higher CO oxidation activity (17). On the other hand, it is expected that H₂ activation on single cationic Pt atoms will be difficult, which makes them ineffective sites for complete oxidation of H₂ to H₂O under mild conditions. Together, isolated cationic Pt atom-based catalysts stand out as promising potential catalysts for CO PROX.

H₂ has been frequently reported to enhance the CO oxidation reaction over Pt-based catalysts (18–23). Some reports implicated a formate species formed on supports that lead to acceleration of the CO oxidation reaction (20, 24). The enhancement was also proposed by others to be due to H₂ facilitating the formation of OH (22, 23). A similar effect of H₂O was also observed, in which the OH group was introduced by H₂O (25–27). It is concluded from these findings that the OH group is crucial to accelerating CO oxidation (26–29). Importantly for the current study, the single- cationic-Pt atom catalysts

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with alkali additives present are coordinated with several OH groups (16, 30, 31), making them a good candidate for CO PROX.

Several techniques have emerged to prepare atomically dispersed catalysts on various supports, such as an ultraviolet-assisted method for photoresponsive metal oxide supports (15, 32), a strong electrostatic adsorption method but with very low loading ($\sim 0.025\%$) (17), and a leaching method to remove metal nanoparticles (NPs) loosely bound on supports, etc. (13, 15). The Flytzani-Stephanopoulos group (16, 30) reported that the alkaline atoms were effective in stabilizing Pt or Au cations by a sheath effect and the catalysts made in this fashion were demonstrated to be remarkably active for WGS, but the protocol involves two steps and has final loading limitations. Pt-O_x-K(Na) sites were produced by K or Na ion stabilizers, which were responsible for the activity of these species on any support, including silica and other inert supports in the WGS reaction. Here, we report a new approach that generates uniform Pt₁-O_x-K(Cs) clusters in aqueous solutions, readily enabling the preparation of high-loading [2 weight % (wt %)] single-Pt atom catalysts, in a single-step impregnation on any support. These single-Pt atom catalysts show a remarkable conversion of CO and O₂ selectivity under excess H₂ conditions. Their structure is stable and can survive high-temperature treatments.

RESULTS AND DISCUSSION

Evidence for the atomic dispersion of Pt in these catalysts comes from a range of techniques. First, x-ray diffraction (XRD) of supported Pt₁-O_x-Cs/SiO₂ shows that there are no observable peaks from Pt NPs (fig. S1). Next, CO was used as the probe molecule in Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to characterize the Pt-based catalysts, and one sharp and symmetric vibrational peak at around 2086 cm⁻¹ is observed for Pt₁-O_x-K/Al₂O₃ (Fig. 1A), which correlates with the vibration of CO linearly adsorbed on cationic single Pt atoms as previously observed (4, 33). As a benchmark, Pt/Al₂O₃ exhibited two broad DRIFTS peaks at around 2050 and 1815 cm⁻¹, which are assigned as linear CO and bridged CO on extended metallic Pt surfaces, respectively (Fig. 1A). In contrast to Pt NPs, the binding between CO and a single Pt atom is much weaker, leading to a smaller CO DRIFT peak due to CO desorption. Furthermore, when the coordination environment of the Pt was investigated by extended x-ray absorption fine structure (EXAFS), only O atoms (no Pt atoms) were found to coordinate with Pt in the first shell, further supporting our hypothesis that the Pt is in single-atom form (Fig. 1B). Last, atomic resolution microscopy was also carried out to study these materials. Aberration corrected-High-angle annular

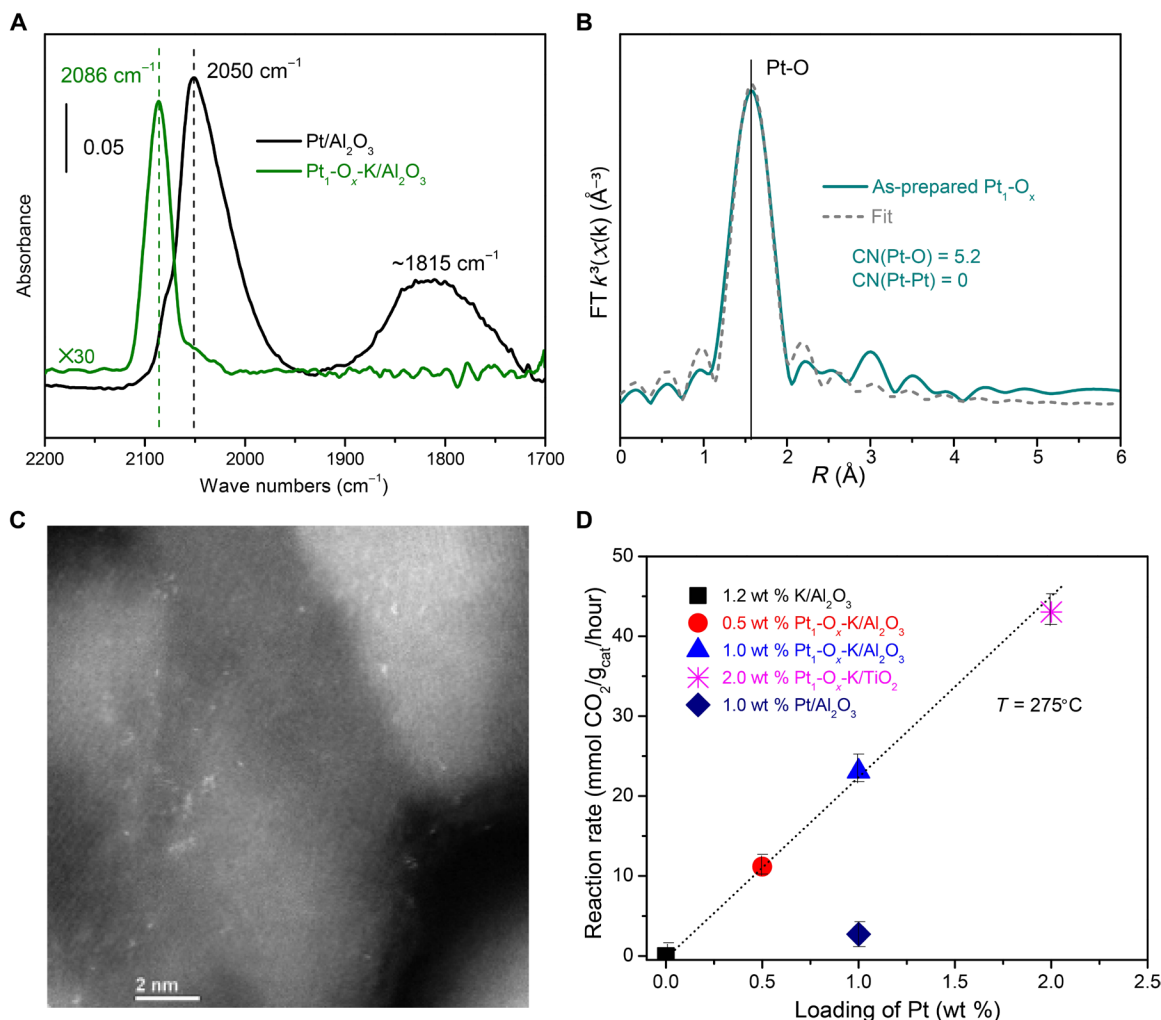


Fig. 1. Characterization of as prepared supported Pt catalysts. (A) CO DRIFTS of Pt/Al₂O₃ and Pt₁-O_x-K/Al₂O₃. (B) EXAFS fitting of as-prepared Pt₁-O_x-K/Al₂O₃. FT, Fourier transform. (C) Representative AC-HAADF-STEM image of Pt₁-O_x-K/Al₂O₃. (D) Plot of WGS activity at 275°C versus Pt loading of different Pt-based catalysts (30 ml/min, 10% CO, 3% H₂O, 100 mg of catalyst loading; each data point was obtained by averaging four data points of stability test).

dark-field–Scanning transmission electron microscopy (AC-HAADF-STEM) images of Pt₁-O_x-K/Al₂O₃ (Fig. 1C and fig. S2) reveal that Pt is atomically dispersed, in agreement with the EXAFS and CO DRIFTS results. Single-atom Pt-O_x-Na(K)-(OH)_y has been demonstrated as the active site for the low-temperature WGS reaction (16, 30, 34). Therefore, WGS was used here as a probe reaction to characterize the catalysts. We found that the WGS reaction rate at 275°C is linearly correlated with the Pt loading for alkaline ion containing catalysts, which confirms that Pt is atomically dispersed up to 2 wt % (Fig. 1D). All the single-Pt atom catalysts that we synthesized and tested were much more active than NP Pt/Al₂O₃ for WGS.

The OH groups, which we later show are the active intermediates in PROX, can be titrated by CO temperature-programmed

reduction (CO-TPR) via the reaction: CO + OH → CO₂ + ½ H₂ (13, 30). The simultaneous production of CO₂ and H₂ with a 2:1 stoichiometric ratio over both Pt₁-O_x-K/Al₂O₃ and Pt/Al₂O₃ was observed, but Pt₁-O_x-K/Al₂O₃ (~75°C) had a much lower light-off temperature than Pt/Al₂O₃ (150°C) (Fig. 2A). This finding indicates that Pt₁-O_x-K/Al₂O₃ has many more active –OH groups than Pt/Al₂O₃ at low temperatures, which corresponds to their exceptional WGS reactivity (fig. S3). Moreover, the surface –OH groups were also analyzed by x-ray photoelectron spectroscopy (fig. S4). The peak centered at ~533.4 eV is ascribed to O 1s of SiO₂ (35), and the other peak located at 531.0 eV is assigned as O 1s in active –OH groups associated with cationic Pt (36), which was barely detected in Pt NPs in the 1.0 wt % Pt/SiO₂ samples. From these data, it can be concluded that the single-Pt atom

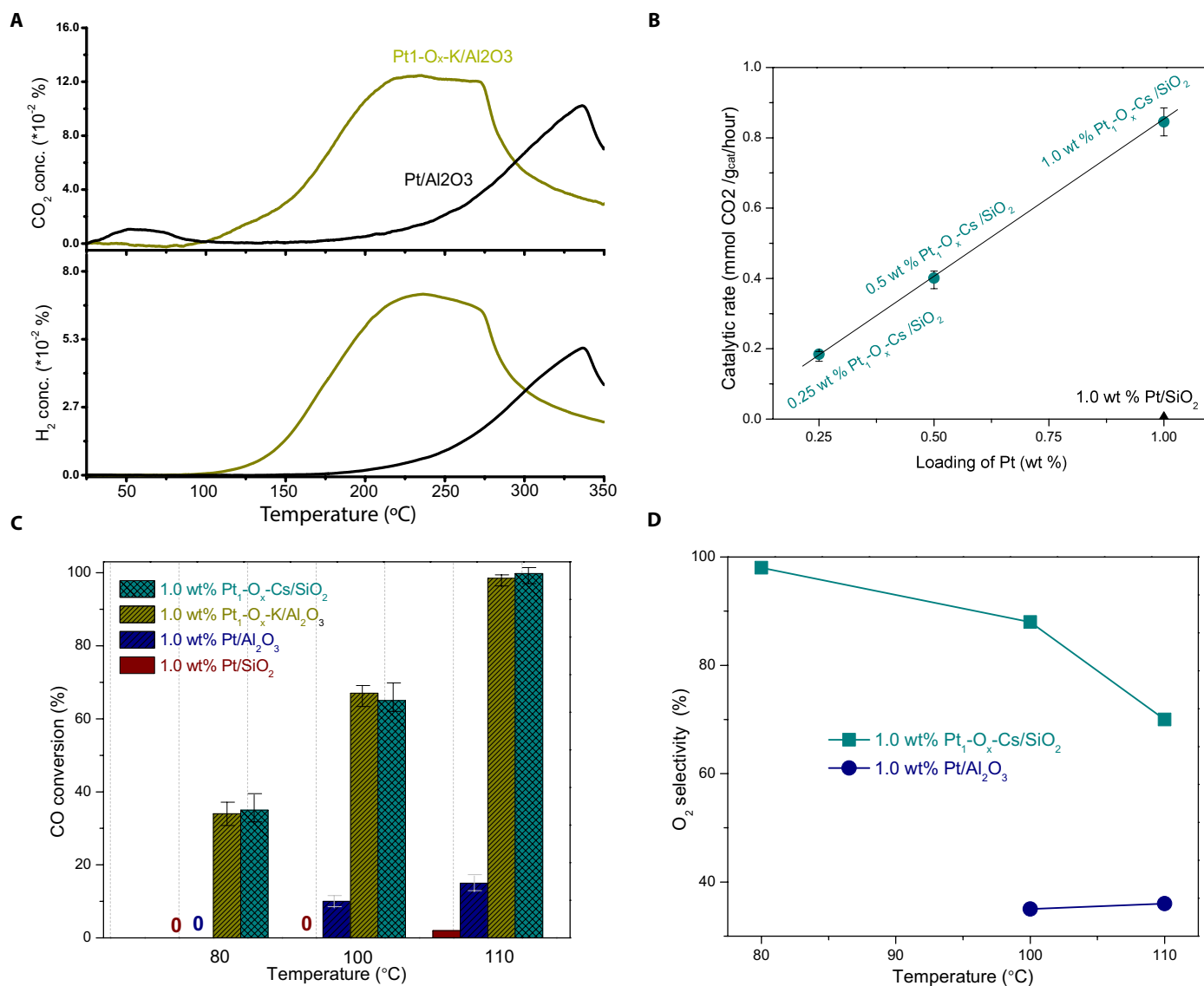


Fig. 2. Catalytic tests of Pt-based catalysts. (A) Production of CO₂ and H₂ from CO-TPR over Pt/Al₂O₃ (black) and Pt₁-O_x-K/Al₂O₃ (green). (B) Activity of CO PROX of supported single-Pt atom and Pt NP catalysts versus Pt loading (reaction conditions: 1% CO, 1% O₂, 40% H₂, 20 ml/min, 100 mg of catalyst, 80°C); each data point is an average of five data points. (C) Conversion of CO at 80°, 100°, and 110°C, respectively, over Pt₁-O_x-Cs/SiO₂, Pt₁-O_x-K/Al₂O₃, Pt/Al₂O₃, and Pt/SiO₂. (D) O₂ Selectivity of Pt/Al₂O₃ and Pt₁-O_x-K/Al₂O₃. All catalysts were calcined at 200°C for 2 hours and then reduced in H₂ at 150°C for 0.5 hours. CO-TPR conditions: 10% CO, 30 ml/min, 100 mg of catalyst, 5°C/min; PROX test conditions for (C) and (D): 1% CO, 1% O₂, 40% H₂, 10 ml/min, 100 mg of catalyst, 5°C/min; the data were obtained by averaging five data points of the stability test.

catalysts were obtained with numerous active OH groups associated with the Pt atoms. Further evidence for these claims is given later in the paper.

To investigate the catalytic performance of the as-synthesized single-Pt atom catalysts, the CO PROX reaction was run over various Pt-based catalysts. For the single-Pt atom catalyst (Fig. 2B), the reactivity increases linearly with Pt loading, consistent with our premise that these atomic $[\text{Pt}_1\text{-O}_x]$ sites are active for CO PROX at low temperatures (fig. S5). In contrast, Pt NPs are the dominant species in the Pt/SiO₂ samples (fig. S6) and exhibited inferior catalytic performance (Fig. 2, B and C). Between 80° and 110°C, there was negligible CO oxidation activity of Pt/SiO₂ and very poor activity of Pt/Al₂O₃. However, their alkali-containing counterparts, 1.0 wt % Pt₁-O_x-Cs/SiO₂ and 1.0 wt % Pt₁-O_x-K/Al₂O₃, exhibit remarkable CO PROX activity in this temperature range (Fig. 2C). Single-Pt atom catalysts show higher CO PROX activity, originating from more accessible active sites (100% atom utilization) (Fig. 1D) and their weak adsorption of CO (Fig. 1A), which has been confirmed by others (17). Even with different inert supports (SiO₂ and Al₂O₃) and different stabilizers (Cs and K), 1.0 wt % Pt₁-O_x-Cs/SiO₂ and Pt₁-O_x-K/Al₂O₃ show very

similar CO PROX activity, which might imply that they share the same active sites, $[\text{Pt}_1\text{-O}_x\text{-(OH)}_y]^-$, and thus a similar reaction pathway for CO PROX at low temperatures. Furthermore, the single-Pt atom catalysts show much higher O₂ selectivity (to CO oxidation), from 99% at 80°C to 70% at 110°C, as compared to the O₂ selectivity of Pt NPs supported on Al₂O₃, which never exceeds 40% at 100° and 110°C (Fig. 2D). In addition, our single-Pt atom catalysts also exhibit higher O₂ selectivity compared to almost all other Pt-based catalysts reported in the literature (table S2). This is mainly due to the metallic Pt surface adsorbing CO so strongly that it hinders CO oxidation at low temperature (4, 8, 9, 19), and the metallic Pt surface readily dissociates and completely oxidizes H₂ to H₂O (37), leading to the loss of the O₂ selectivity.

The cyclic stability test of CO PROX on the 1.0 wt % Pt₁-O_x-Cs/SiO₂ catalyst in Fig. 3A shows that the single-atom Pt catalyst does not deactivate during the multitemperature steps in an ascending and descending mode with steady-state holds of 2 hours at each temperature. A 60-hour stability test at 110°C was also carried out to examine the durability of Pt₁-O_x-Cs/SiO₂ (fig. S7). The x-ray absorption near-edge structure (XANES) spectra of the as-prepared and in

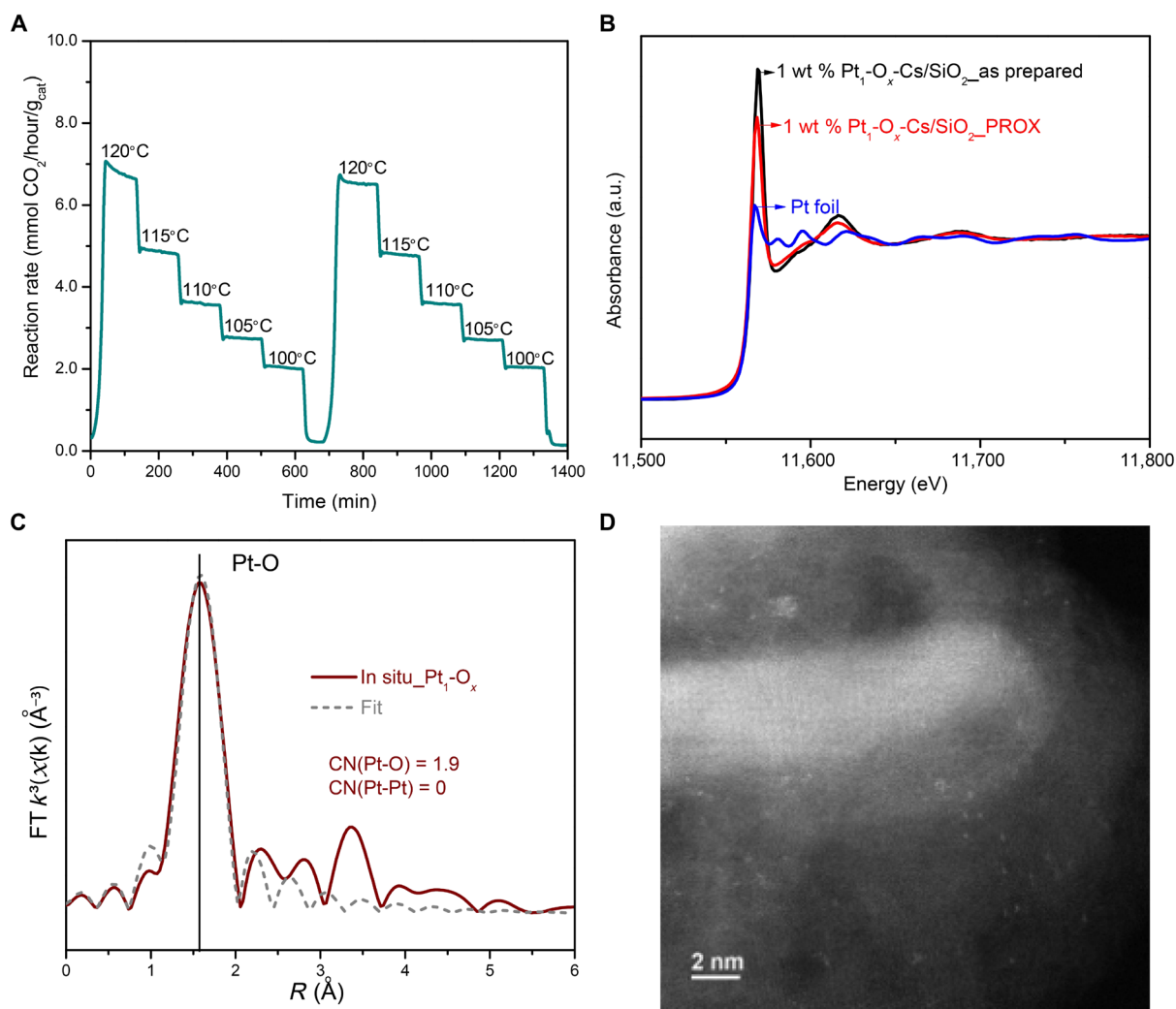


Fig. 3. Stability of $[\text{Pt}_1\text{-O}_x\text{-(OH)}_y]^-$ species for CO PROX reaction. (A) Cyclic stability test of 1.0 wt % Pt₁-O_x-Cs/SiO₂ from 373 to 393 K, 1% CO, 1% O₂, 40% H₂, 50 ml/min, 100 mg of catalyst, 5°C/min. (B) XANES spectra of as-prepared 1.0 wt % Pt₁-O_x-Cs/SiO₂ and operando under CO PROX reaction conditions; 1% CO, 1% O₂, 40% H₂, 20 ml/min, reaction temperature: 120°C. a.u., arbitrary unit. (C) EXAFS fitting of 1.0 wt % Pt₁-O_x-Cs/SiO₂ under the reaction conditions in (B). (D) AC-HAADF-STEM images of spent 1.0 wt % Pt₁-O_x-K/Al₂O₃; reaction conditions: 1% CO, 1% O₂, 40% H₂, 20 ml/min, reaction temperature: 120°C, 1 hour.

operando evaluated 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂ catalyst reveal that the charge state of Pt in 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂ decreases from around +4 but crucially does not become metallic Pt under reaction conditions (Fig. 3B), which is consistent with the WGS-reported EXAFS results for single-atom Pt catalysts (16). Correspondingly, the coordination number of the Pt center changes from 5.2 (Fig. 1C) to 1.9 (Fig. 3C) as obtained from EXAFS fitting of the 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂ catalyst sample under operando conditions (table S1), revealing that the cluster containing the Pt atom evolves to be less coordinated (more open) under reaction conditions. The stability of the single-Pt atom species was further demonstrated by AC-HAADF-STEM images and CO DRIFTS of 1.0 wt % Pt_{1-x}O_x-K/Al₂O₃ used in CO PROX (Fig. 3D and figs. S5 and S8), showing that single Pt atoms were preserved after the reaction at 110°C.

Kinetic tests for the WGS reaction over the different single-Pt atom catalysts confirmed that all Pt catalysts tested here are atomically dispersed (Fig. 4A) because the apparent activation energy (E_{app}) of 71 kJ/mol is the same for all. This E_{app} is also the same as values re-

ported in the literature (16, 30, 34), indicating the presence of the same active sites for WGS.

It has been frequently reported that the addition of H₂O in the reactant stream can boost CO oxidation for Pt-based catalysts (25, 27–29, 33). However, we find negligible enhancement of CO oxidation by introducing H₂O over 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂ (Fig. 4B). In contrast, H₂ activates the Pt site and enables the production of OH groups, two ingredients for making a remarkably active CO oxidation catalyst. The involvement of –OH in the course of CO PROX is further demonstrated below.

The kinetic study of CO PROX conducted over the single atom Pt catalysts used here is summarized in the Arrhenius-type plot for CO oxidation over 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂ with and without H₂ (Fig. 4C). One can also see from the plot that the catalytic performance of 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂ and Pt_{1-x}O_x-K/Al₂O₃ was obtained, as expected, and provides further evidence for the lack of a support effect. The same apparent activation energy (E_{app}) of CO PROX on

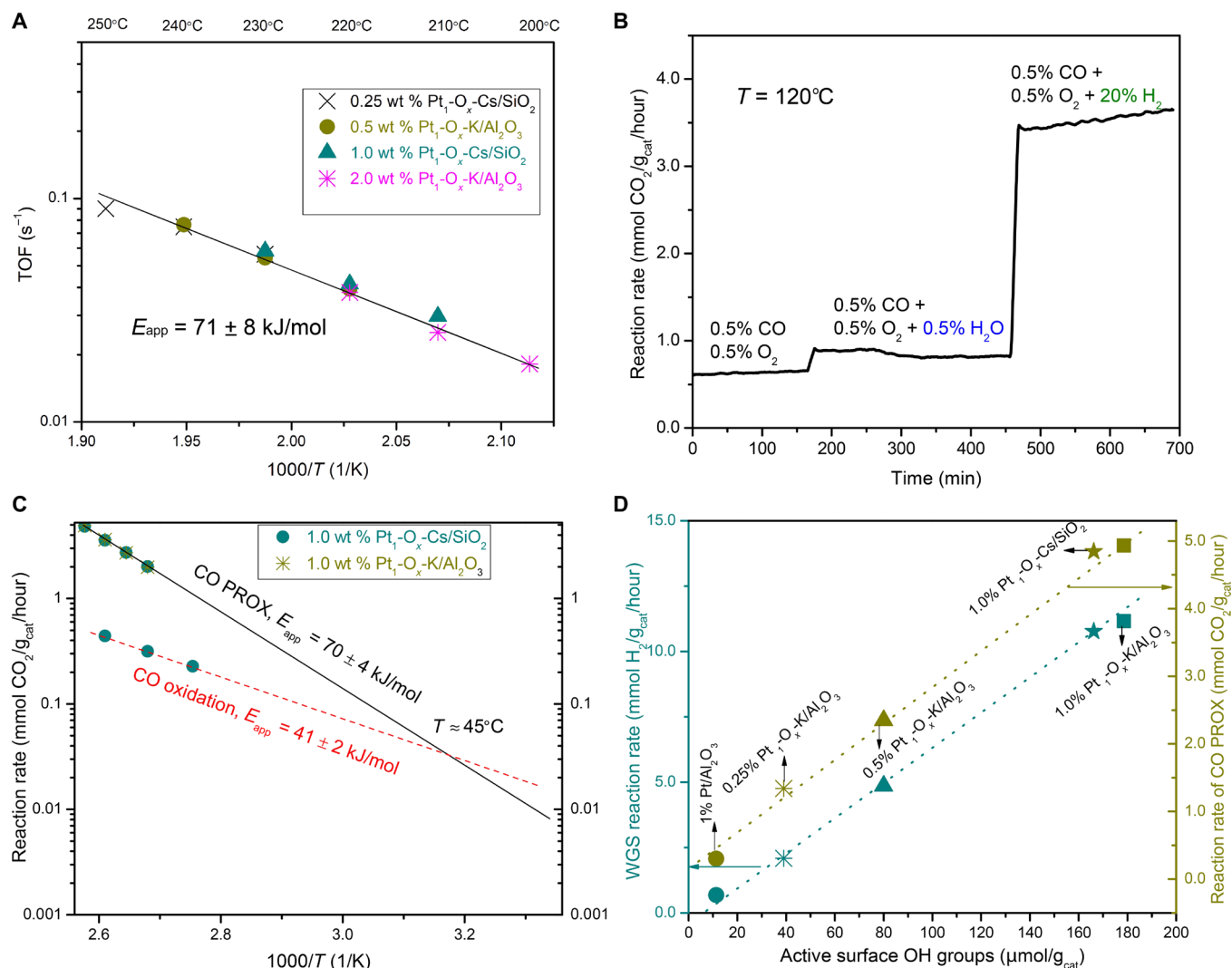
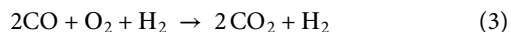
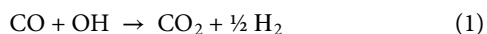


Fig. 4. Mechanistic study of CO PROX over the single-Pt atom catalysts. (A) Arrhenius plot of the WGS turnover frequency (TOF) over various single-Pt atom catalysts. (B) Promotion effect of H₂O and H₂ for CO oxidation over 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂. (C) Arrhenius plot of CO oxidation with and without H₂ over 1.0 wt % Pt_{1-x}O_x-Cs/SiO₂. (D) Linear plot of WGS reactivity and CO PROX reactivity versus active surface OH groups. WGS test conditions: 10% CO, 3% H₂O, 30 ml/min, 100 mg of catalyst loading, 250°C (data were obtained by averaging three stability test results). CO PROX reaction conditions: 1% CO, 1% O₂, 40% H₂, 50 ml/min, 50 mg of catalyst, 5°C/min, 115°C (data were obtained by averaging five stability tests). CO oxidation reaction conditions: 1% CO, 1% O₂, 50 ml/min, 50 mg of catalyst, 5°C/min.

both catalysts, 70 kJ/mol, is close to the E_{app} (~71 kJ/mol) found for WGS (Fig. 4A) and over various other Pt-based catalysts (13, 16, 30). These results suggest that they may share the same reaction step (1), $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \frac{1}{2} \text{H}_2$. To support this hypothesis, the activity of WGS and CO PROX as a function of the number of OH groups (derived from CO-TPR) was studied. A linear correlation was obtained for all Pt-based catalysts tested (Fig. 4D), which again confirms the crucial role of $-\text{OH}$ in CO PROX. The participation of surface $-\text{OH}$ groups was demonstrated by the regeneration of $-\text{OH}$ by H_2 and O_2 treatment via reaction (2) (fig. S9). The generation of $-\text{OH}$ from H_2 and O_2 has been extensively studied (38, 39), supporting this finding. Therefore, the overall reaction of CO oxidation in the presence of H_2 over single-Pt atom catalysts is proposed to proceed via reaction (3), in which H_2 works as a cocatalyst by making active OHs (2) that then react with CO and regenerate H_2 as seen in reaction (1)



Labeling experiments, in which H_2 was substituted by D_2 , were conducted to further probe the reaction mechanism using by CO-TPR experiment (fig. S9). Specifically, OH associated with the Pt atoms was first depleted by cyclic CO-TPR, and then introduction of O_2 and D_2 to the catalyst at mild conditions was performed to regenerate these hydroxyl groups. As one would expect, OD should be generated by reaction (2), and indeed, CO_2 and D_2 appeared as products with a 2:1 ratio, consistent with our reaction scheme above.

When H_2 is absent, the E_{app} of dry CO oxidation decreased to 41 kJ/mol (Fig. 4C), close to the reported value for dry CO oxidation over Pt-based catalysts (40), but with a notable loss in activity, which implies that the introduction of H_2 changes the CO oxidation reaction pathway. Extending the Arrhenius-type plots of CO oxidation and CO PROX reactions reveals that the intersection is at 45°C, meaning that below 45°C, the activity of CO oxidation without H_2 would surpass CO PROX.

In conclusion, high-content single-Pt atom catalysts can be prepared with alkali stabilizers by a new facile single-step method first reported here, and their activity and selectivity does not depend on the choice on the support. Their impressive catalytic performance originates from a large amount of accessible $[\text{Pt}_1-\text{O}_x]$ active sites (100% atom utilization), of low chemical valence during reaction, that remain positively charged during long stability tests. The single Pt atom in our catalysts can activate H_2 and O_2 to generate $-\text{OH}$, which boosts CO oxidation via the WGS reaction pathway. This work paves the way to synthesize stable, high-loading single-atom catalysts via the alkali stabilizer strategy. These new catalysts are promising candidates for achieving high CO conversion and O_2 selectivity for the CO PROX reaction, which is an increasingly attractive and energy efficient technology.

MATERIALS AND METHODS

The facile synthesis involves adding $\text{H}_2\text{Pt}(\text{OH})_6$ powder into an alkaline solution (KOH or CsOH) at 80°C with 2% O_2 (bal. He) purge

and constant stirring for 8 to 10 hours until a stable yellow transparent solution was obtained. The solution was carefully sealed and stored in the dark. Supported $[\text{Pt}_1-\text{O}_x]/\text{SiO}_2$ (Al_2O_3) samples were prepared by incipient wetness impregnation of the selected support; the samples were dried at 70°C under vacuum and then treated with 10% H_2 in He at 150°C before testing and characterization.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/6/25/eaba3809/DC1>

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