Diphosphine-Protected \( \text{Au}_{22} \) Nanoclusters on Oxide Supports Are Active for Gas-Phase Catalysis without Ligand Removal

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Supporting Information

ABSTRACT: Investigation of atomically precise Au nanoclusters provides a route to understand the roles of coordination, size, and ligand effects on Au catalysis. Herein, we explored the catalytic behavior of a newly synthesized \( \text{Au}_{22}(L^8)_6 \) nanocluster \((L = 1,8\text{-bis(diphenylphosphino)} \text{ octane}) \) with in situ uncoordinated Au sites supported on \( \text{TiO}_2 \), \( \text{CeO}_2 \), and \( \text{Al}_2\text{O}_3 \). Stability of the supported \( \text{Au}_{22} \) nanoclusters was probed structurally by in situ extended X-ray absorption fine structure (EXAFS) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and their ability to adsorb and oxidize CO was investigated by IR absorption spectroscopy and a temperature-programmed flow reaction. Low-temperature CO oxidation activity was observed for the supported pristine \( \text{Au}_{22}(L^8)_6 \) nanoclusters without ligand removal. Density functional theory (DFT) calculations confirmed that the eight uncoordinated Au sites in the intact \( \text{Au}_{22}(L^8)_6 \) nanoclusters can chemisorb both CO and \( \text{O}_2 \). Use of isotopically labeled \( \text{O}_2 \) demonstrated that the reaction pathway occurs mainly through a redox mechanism, consistent with the observed support-dependent activity trend of \( \text{CeO}_2 > \text{TiO}_2 > \text{Al}_2\text{O}_3 \). We conclude that the uncoordinated Au sites in the intact \( \text{Au}_{22}(L^8)_6 \) nanoclusters are capable of adsorbing CO, activating \( \text{O}_2 \), and catalyzing CO oxidation reaction. This work is the first clear demonstration of a ligand-protected intact Au nanocluster that is active for gas-phase catalysis without the need of ligand removal.

KEYWORDS: Gold nanoclusters, ligands, uncoordinated sites, CO oxidation, oxide support

Gold nanoclusters have attracted intensive research interest because they can be considered an ideal model system for understanding the intriguing catalytic properties of gold nanoparticles with molecular- and atomic-level details.\(^1\)\(^−\)\(^3\) This is attributed to the unique electronic and geometric structure, atomic precision, and uniform molecular size of the ligand-protected gold nanoclusters.\(^4\)\(^−\)\(^7\) They are often designated as \( \text{Au}_n \text{R}_m \), where \( n \) and \( m \) denote the numbers of gold atoms and R ligands (mostly thiolate, SR), respectively. Gold nanoclusters have shown great promise in various reaction systems including oxidation, hydrogenation, carbon—carbon coupling, electrocatalysis, and photocatalysis. These reactions were mostly carried out in the liquid phase under mild conditions and, thus, can take advantage of the uniqueness of the intact gold nanoclusters. Gas-phase catalysis was much less explored with Au nanoclusters, which need to be dispersed on a support. The role of the ligands on the catalytic performance of Au nanoclusters in gas-phase reactions is widely debated. Although most studies\(^8\)\(^−\)\(^14\) showed a negative role of the ligands because of their blockage of the active Au sites, some\(^15\)\(^−\)\(^17\) suggested the presence of ligands does not prevent the Au nanoclusters from catalyzing reactions. A recent study\(^18\) even showed a promotional effect of ligands on the gas-phase catalysis of Au nanoclusters, although the underlying mechanism was not elaborated. As most studies indicated, removal of the ligands on the Au nanoclusters provides “exposed” or so-called coordinatively unsaturated (cus) Au sites and, thus, improved catalytic performance in gas-phase reactions. However, stripping off the ligands can inevitably result in significant changes to the electronic or geometric structure of the Au nanoclusters and introduce complex metal—support interactions,\(^8\)\(^,\)\(^13\)\(^,\)\(^14\) which makes the model catalysts of Au nanoclusters less straightforward for fundamental understanding. It is, thus, highly desirable to synthesize ligand-protected Au nanoclusters with the presence of cus Au sites, i.e., some of the surface Au atoms

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are free from coordination with the ligands. Stimulated by the discovery of the Au20 pyramid in the gas phase,19 some of us have endeavored to synthesize it in bulk form with uncoordinated surface sites for in situ catalysis.20,21 Such an Au nanocluster was recently achieved22 with diphosphine ligands, i.e., a Au22 nanocluster coordinated by six bidentate diphosphine ligands: 1,8-bis(diphenylphosphino) octane (L8 for short). The Au22(L8)6 nanocluster was found to consist of two Au11 units linked together by four L8 ligands, in which the eight gold atoms at the interface of the two Au11 units are not coordinated by any ligands (see Figure S1 for the structural model). It is anticipated that these Au atoms may be utilized as in situ active sites for catalysis without the need of ligand removal.23

In the current study, we investigated gas-phase CO oxidation over supported Au22(L8)6 nanoclusters. The structure, morphology, and nature of surface sites of the supported Au22(L8)6 nanoclusters were characterized in detail via scanning transmission electron microscopy (STEM), extended X-ray absorption fine structure (EXAFS), and in situ infrared spectroscopy. We found that regardless of the supports used (TiO2, CeO2, or Al2O3), the intact Au22(L8)6 nanoclusters readily show low-temperature catalytic activity for CO oxidation, implying that the Au atoms are indeed active for catalysis. This was substantiated by the ability of the Au22(L8)6 nanoclusters to adsorb CO molecules, as demonstrated by IR spectroscopy and reinforced by density functional theory (DFT). The combined efforts show convincingly that the Au atoms on supported, intact Au22(L8)6 are active for low-temperature catalytic CO oxidation, thereby demonstrating that ligand removal is not necessary for some gold nanoclusters to be catalytically active and that creating in situ Au atoms should be a promising direction in nanocluster synthesis for catalytic applications.

Characterization of Free-Standing and Supported Au22(L8)6 Nanoclusters. The free-standing Au22(L8)6 nanoclusters were synthesized using the method reported previously22 and characterized by both UV–vis–near-infrared (NIR) absorption (Figure S2A) and mass spectrometry (Figure S2B) analysis. The UV–vis–NIR spectrum exhibits a main absorption band at ~457 nm, similar to that reported for pure Au22(L8)6 nanoclusters in previous work.22 The main m/z peaks at 3616 and 2410 in the mass spectrum corresponds to [Au22(L8)6 + 4H] species in +2 and +3 charge states, respectively. The isotopic patterns (insert in Figure S2B) for the peak at 3616 agree well with the expected isotopic distribution.22 Both the UV–vis–NIR and electrospray ionization mass spectrometry (ESI-MS) results demonstrate

Figure 1. (A,B) HAADF-STEM images of as-synthesized Au22(L8)6–TiO2 in different magnifications. CO oxidation light-off curves for different temperature treated Au22(L8)6–TiO2 samples (C) and the as-synthesized Au22(L8)6 supported on TiO2, CeO2, and Al2O3 (D). The light-off curve from as-synthesized Au25(SR)18–CeO2 is also included in the two figures for comparison.
the successful synthesis of atomically precise Au$_{22}$(L$^8$)$_6$ nanoclusters with monodispersity. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the as-synthesized Au$_{22}$(L$^8$)$_6$-TiO$_2$ sample are shown in panels A and B of Figure 1 with different magnifications. The Au nanoclusters are well dispersed on the TiO$_2$ surface with an average size of ~1.4 nm. Individual Au atoms are discernible in the nanoclusters in the higher magnification image (Figure 1B). These images clearly show that the Au$_{22}$(L$^8$)$_6$ nanoclusters are highly dispersed on TiO$_2$ surface without obvious agglomeration.

**Observation of CO Oxidation over Supported Au$_{22}$(L$^8$)$_6$, Au$_{22}$(L$^8$)$_6$-TiO$_2$** samples that were O$_2$-pretreated at different temperatures were tested for CO oxidation in the temperature range 295–450 K, and the CO oxidation light-off curves are shown in Figure 1C. The as-synthesized Au$_{22}$Ti-295 sample shows mild CO oxidation activity starting at room temperature and increased activity at elevated temperatures. This is drastically different from our previously studied as-synthesized Au$_{22}$ nanoclusters (shown in the figure for comparison), where surface Au atoms are fully coordinated with thiolate ligands and showed no CO oxidation activity. The clear contrast indicates that the *cus* Au atoms in the Au$_{22}$(L$^8$)$_6$ nanoclusters are readily active for CO oxidation at low temperature. With the O$_2$-treatment temperature of the Au$_{22}$Ti-295 sample, CO oxidation activity increases accordingly, a similar trend being observed for the Au$_{22}$ nanoclusters. This is attributable to the gradual removal of the surface ligands and simultaneous liberation of more *cus* Au sites for catalysis, as supported by the following EXAFS and IR studies.

It is notable that the turnover frequency (TOF) of the *cus* Au atoms in the as-synthesized Au$_{22}$Ti-295 sample is calculated to be ~0.02 s$^{-1}$ for CO oxidation at 303 K, comparable to the value for a typical Au–TiO$_2$ nanocatalyst (0.023 s$^{-1}$). The number of *cus* Au sites used for the TOF calculation was obtained in the following way: the maximum possible number of surface Au sites was approximated as being 91% of the total gold atoms because 20 out of 22 Au atoms in the Au$_{22}$(L$^8$)$_6$ nanoclusters are exposed on the outer surface. From this maximum possible number of sites, the number of accessible sites for the as-synthesized Au$_{22}$Ti-295 sample was then calculated based on the CO band area observed during the IR measurements described below.

To verify whether the observation made on Au$_{22}$(L$^8$)$_6$-TiO$_2$ is general, we also loaded Au$_{22}$(L$^8$)$_6$ onto CeO$_2$ and Al$_2$O$_3$ supports and compared the as-synthesized samples for CO oxidation. The CO oxidation light-off curves for the three samples are compared in Figure 1D along with the as-synthesized Au$_{22}$,(SR)$_{18}$-CeO$_2$ sample. As a note, the CO oxidation activity is similar for these samples pretreated at room temperature with either 5% O$_2$–He or pure He. The Au$_{22}$Ce-295 sample shows much higher low-temperature CO oxidation activity than Au$_{22}$Ti-295. Although the Au$_{22}$Al-295 sample is much-less-active for CO oxidation than Au$_{22}$Ti-295 and Au$_{22}$Ce-295, it indeed shows some activity when the reaction temperature rises, especially in comparison to the as-synthesized Au$_{22}$,(SR)$_{18}$-CeO$_2$ sample, which is essentially not active at all in the tested temperature range. The result clearly supports that the *cus* Au atoms in the as-synthesized Au$_{22}$(L$^8$)$_6$ nanoclusters are readily active for low-temperature CO oxidation. Furthermore, the activity is greatly impacted by the oxide supports because the reducible oxides (CeO$_2$ and TiO$_2$) supports lead to higher activity than the nonreducible Al$_2$O$_3$. This is similar to the general observation made on supported Au nanoparticles, where the nature of the oxide support has been shown to be the dominant factor affecting the catalysis by Au nanoparticles. The underlying reason for the support effect is further discussed below (the Reaction Mechanisms section).

**State of the L$^8$ Ligands in the Supported Au$_{22}$(L$^8$)$_6$ Clusters.** One pressing question about the as-synthesized Au$_{22}$(L$^8$)$_6$-TiO$_2$ is whether the Au nanoclusters are intact, i.e., whether the diphosphine ligands are partially removed upon dispersion on a TiO$_2$ surface. In situ extended X-ray absorption fine structure (EXAFS) was utilized to monitor the Au–P bond in the different temperature-treated samples, and the spectra are shown in Figure 2. Spectra from an unsupported Au$_{22}$(L$^8$)$_6$ nanocluster sample, the Mintek Au–TiO$_2$ standard, and gold foil are also shown for comparison. The Au–P single scattering peak has an apparent, nonphase-shift corrected position at 1.91 Å for the unsupported Au$_{22}$ nanoclusters. Fitting the spectrum for the unsupported Au$_{22}$ nanoclusters using the ARTEMIS program produces an actual Au–P distance of 2.28 Å. The Au–P coordination number (CN) was determined to be 0.5, which is in excellent agreement with actual value of 0.55. Although there appears to be a small shift in the Au–P peak to a longer distance when the Au$_{22}$(L$^8$)$_6$ is supported on TiO$_2$, possibly due to the interaction of the nanoclusters with the TiO$_2$ surface, the fit to the data indicated that the Au–P distance is unchanged. The CN is also unchanged. This suggests that the Au nanoclusters dispersed on the TiO$_2$ surface are similarly coordinated with the diphosphine ligands as in the unsupported case. The structure of the Au$_{22}$ core in the as-synthesized Au$_{22}$(L$^8$)$_6$-TiO$_2$ also largely resembles that of the unsupported nanoclusters as evident from the similar features of the Au–Au peaks in 2–3 Å range. The fit for the Au–Au peaks in the unsupported nanoclusters indicates an average Au–Au distance of 2.71 Å. The average distance for the nanoclusters supported on TiO$_2$ is 2.74 Å. The average Au–Au distance in these Au$_{22}$ nanoclusters is smaller than the Au–Au distance in either the nanoparticle supported on TiO$_2$ in the Mintek standard or in the Au foil, which were determined by EXAFS to be 2.84 and 2.87 Å, respectively. Note that the peak near 2.2 Å for the Au

![Figure 2. EXAFS spectra of various Au samples and Au$_{22}$(L$^8$)$_6$-TiO$_2$ sample pretreated at different temperatures in O$_2$. Spectra from Au foil and Mintek Au–TiO$_2$ catalyst are also shown as references.](image-url)
The growth of Au nanoclusters at temperature above 573 K is likely associated with the removal of the diphosphine ligands. This is supported by the thermal gravity analysis (TGA) results of unsupported \( \text{Au}_{22}(L^8)_6 \) nanoclusters (Figure S5A), where the major mass loss occurs at 587 K. The weight loss of \(~40\%\) is consistent with the complete removal of the \( L^8 \) diphosphine ligands. IR spectra collected on the \( \text{Au}_{22}(L^8)_6 \) nanocluster after \( O_2 \) treatment at different temperatures are shown in Figure S5B. C–H stretching modes are observed at 3067 (aromatic C–H), 2963, 2927, and 2858 cm\(^{-1}\) (aliphatic C–H) due to the \( L^8 \) ligands. These features are fairly weak on the as-synthesized sample, possibly due to the presence of water on the TiO\(_2\) surface, similar to the observation on an as-synthesized \( \text{Au}_{22}(\text{SR})_6\)–CeO\(_2\) sample.\(^8\) These C–H stretching modes are fairly stable in intensity in the temperature range from 423–523 K but show a certain degree of decline after 573 K treatment and disappear after 673 K treatment. This trend is in good agreement with the TGA result, suggesting a treatment temperature above 573 K is needed to fully remove the \( L^8 \) ligands from the \( \text{Au}_{22}(L^8)_6\)–TiO\(_2\) sample.

**Nature of the Au Sites on the \( \text{Au}_{22}(L^8)_6 \) Cluster Surface.** IR spectroscopy combined with CO adsorption was employed to probe the nature of the \( \text{Au} \) sites available in the as-synthesized \( \text{Au}_{22}(L^8)_6\)–TiO\(_2\) sample. As shown in Figure 3A, CO adsorption on the as-synthesized sample results in an IR band at 2107 cm\(^{-1}\), ascribed to CO adsorbed on metallic \( \text{Au} \) sites.\(^28\)–\(^30\) This observation clearly demonstrates that the \( \text{Au} \) sites in the intact nanoclusters can indeed adsorb CO molecules. Furthermore, the adsorbed CO species can be readily oxidized by \( O_2 \) at room temperature, as is evident from Figure 3B. The IR band at 2107 cm\(^{-1}\) decreases in intensity and shifts slightly to higher wavenumbers when the sample was exposed to \( O_2 \) purging at room temperature. This band vanishes after \( O_2 \) purging for 8 min, indicating complete oxidation of the adsorbed CO species. A similar observation was also made on the as-synthesized \( \text{Au}_{22}(L^8)_6\)–CeO\(_2\) sample, as shown in Figure S6. Therefore, the \( \text{Au} \) sites in the intact \( \text{Au}_{22}(L^8)_6\) nanoclusters can not only adsorb CO molecules but also activate and oxidize them in the presence of \( O_2 \) at room temperature, supporting the observed activity of the as-synthesized sample in CO oxidation, as shown in Figure 1. It is interesting to note that the nature of the \( \text{Au} \) sites (metallic) in \( \text{Au}_{22}(L^8)_6 \) nanoclusters is quite different from that of the \( \text{Au} \) sites (cationic) on slightly dethiolated \( \text{Au}_{25} \) clusters (CO band at 2150 cm\(^{-1}\)).\(^5\) This is directly related to the electron-donating diphosphine ligands on the \( \text{Au}_{22} \) nanoclusters compared to the electron-withdrawing thiolate ligands on the \( \text{Au}_{25} \). A recent DFT study\(^25\) shows that the eight \( \text{Au} \) atoms are barely affected by the charge transfer from the phosphine ligands to the \( \text{Au} \) nanoclusters and thus close to neutral charge.
atoms in the Au_{22} nanocluster are exposed completely after the treatments at 573 K and above (Figure 3A). The exposure of the Au sites after the ligand removal, resulting in charge transfer from the phosphine and thiolate ligands. Again, the shifting trend of the Au+ persists in the presence of O_2 at room temperature, consistent with the high stability and lower reactivity of CO adsorbed on Au+ sites. The contrast clearly suggests that the partially positively charged Au sites (Au^{δ+} (0 < δ < 1)) are the major active sites for CO oxidation on Au^{δ+} (0 < δ < 1) sites has reacted with oxygen. The IR band at 2162 cm^{-1} due to CO–Au+ persists in the presence of O_2 at room temperature, consistent with our observed IR band at 2107 cm^{-1}.

The observations made in the TGA and IR spectra in Figure S5 (ligand removal at 573 K and above) seem to contradict those made in the EXAFS spectra in Figure 2 (Au–P breakage between 423 and 523 K) and IR of CO probing in Figure 3A (continuous increase of Au sites availability up to 673 K). This can be reconciled by the situation in which the diphosphine ligands are gradually stripped off the Au sites at temperature above 423 K yet the ligand molecules still remain on the catalyst surface, possibly on the oxide support due to the high boiling point. This is supported by the TGA profile from a physical mixture of TiO_2 and the L_8 ligand (Figure S9), where the maximum weight loss occurs at 595 K. Thus, it is likely the P ligands start to vaporize at temperature above 573 K, giving the TGA weight loss and the loss of C–H modes in the IR spectra (Figure S5) above 573 K in the Au_{22}(L_8)_6–TiO_2 sample.

Reaction Mechanisms. To reveal the reaction mechanisms of the low-temperature CO oxidation over the Au_{22}(L_8)_6–TiO_2 catalyst, we chose the as-synthesized sample because it already had the cas Au sites and the ligands were still attached. It is evident from the above IR work that CO is adsorbed on the cas Au sites and can be oxidized by co-feeding O_2. To investigate how O_2 is activated for CO oxidation, we carried out an isotopic labeling experiment by co-feeding CO and ^18O_2 over the 295 K-treated Au_{22}(L_8)_6–TiO_2 sample. The evolved CO_2...
isotopomers were followed by online QMS as a function of reaction time, and the profiles are shown in Figure 4A. CO₂ production is dominated by C¹⁶O¹⁶O in the temperature range 300−450 K, while a small contribution from C¹⁸O¹⁸O is observed at temperatures above 360 K and C¹⁸O¹⁸O production is negligible. The observation of only C¹⁶O¹⁶O at the initial stage of CO oxidation light-off and its dominance over the tested temperature range indicate that CO is reacting with Ti¹⁶O₂ lattice oxygen to form CO₂, i.e., going through a Mars−van Krevelen (MvK) mechanism.

This MvK mechanism implies that the intact Au₂₂(L⁸)₆ nanoclusters have to be in close proximity to the TiO₂ surface so that the adsorbed CO on the nanoclusters can readily react with the lattice oxygen of the oxide support. The observation of the redox mechanism is supposedly a result of ligand relaxation. That is, the conformations and tilting angles of the K groups on the phosphorus atoms of the ligands on the Au₂₂ surface can adapt to the TiO₂ support to bring the Au gold atoms close to the TiO₂ surface to enable the MvK mechanism. This argument is partly supported by the STEM observation (Figure 1A) that many of the Au₂₂ nanoclusters are found to locate at the valleys and boundaries between TiO₂ particles, where the ligand−TiO₂ interaction is strong, and hence, the ligand relaxation is expected to be the greatest, allowing the Au atoms to be close to the TiO₂ surface. For the Au₂₂ nanoclusters on the terraces of TiO₂, the curvature and the presence of steps and corners on TiO₂ particles may also offer close proximity of lattice oxygen atoms to the Au atoms in the Au₂₂ nanoclusters. The postulation here is only qualitative in nature, and the detailed mechanism warrants further investigation on how in general ligand-protected metal nanoclusters interact with an oxide surface.

The growth of C¹⁶O¹⁸O at higher temperature is thus due to the reaction of CO with lattice¹⁸O replenished by the gas-phase¹⁸O₂. Once oxygen vacancies on TiO₂ are created via CO reduction, gas-phase¹⁸O₂ can adsorb on the vacancy sites to form various species such as superoxide and peroxide.3⁷ It was shown that these adsorbed O₂ species can readily dissociate and refill the oxygen vacancies at elevated temperatures so that the CO oxidation cycle is complete.

The demonstrated MvK mechanism for low-temperature CO oxidation can well explain the large activity difference in CO oxidation over Au₂₃(L⁸)₆ brought about by varying the oxide support (Figure 1D). The higher reducibility of CeO₂ than TiO₂ (see Figure S10 for the CO−TPR profiles) is in line with the better activity of Au₂₂Ce-295 than Au₂₂Ti-295. MvK mechanism for CO oxidation was also observed on other gold nanoclusters supported on oxides.⁸,3⁸ Because Al₂O₃ is nonreducible, the MvK mechanism involving lattice oxygen is not possible for CO oxidation over Au₂₂Al-295. The weak activity for CO oxidation on Au₂₂Al-295 can be attributed to a possible role of the Langmuir−Hinshelwood (L−H) mechanism on the Au sites in the Au₂₂(L⁸)₆ nanoclusters, where both CO and O₂ are activated and reacted. This kind of L−H route was also observed to play a minor role in CO oxidation over a dethiolated Au₂₅(SR)₁₈−CeO₂ catalyst.⁸ The L−H mechanism is further confirmed with an isotope labeling experiment. As shown in Figure 4B, CO oxidation with¹⁸O₂ over the 295 K-treated Au₂₂(L⁸)₆−Al₂O₃ sample produces dominantly C¹⁶O¹⁸O and C¹⁸O¹⁶O, implying the ability of the Au sites in intact Au₂₂(L⁸)₆ nanoclusters to activate and dissociate O₂ molecules. The production of C¹⁶O¹⁸O is likely due to the presence of reactive surface hydroxyl groups that can react with adsorbed CO on Au₂₂(L⁸)₆ nanoclusters to produce CO₂, which has been previously observed for CO oxidation on Al₂O₃-supported Au nanoparticles.³⁹

To further elucidate the catalytic mechanisms of CO oxidation, we investigated CO adsorption on the Au₂₂(L⁸)₆ nanocluster with DFT. We found that CO only adsors on the eight Au atoms (Figure 5A). Due to the symmetry of the cluster, the eight Au atoms can be divided into four groups. Figure 5B shows the most stable CO adsorption site on one of the Au atoms with an adsorption energy of −0.98 eV, indicating strong adsorption of CO. After adsorption, the C−O bond length slightly increases to 1.167 Å from the gas-phase value of 1.143 Å. For the other three groups of Au atoms, the adsorption energies are −0.92, −0.90, and −0.79 eV; in contrast, CO adsorption on the non-cus Au sites is much weaker (∼−0.22 eV). This indicates that cus Au atoms have a strong ability to adsorb and activate CO molecules for CO oxidation. To test if the cus Au sites can activate O₂, we studied...
the coadsorption of CO and O₂ on the cluster. We found that the adsorption of O₂ is very favorable on the CO-adsorbed Au₂₅(L⁸)₆ nanocluster with an adsorption energy of −1.44 eV (Figure 5C). In addition, the O=O bond is significantly weakened after adsorption, as is evident from its lengthening to 1.352 Å in comparison with the gas-phase value of 1.236 Å. Hence, our DFT results show that the Au₄ sites of the Au₂₅(L⁸)₆ nanocluster can coadsorb CO and O₂ with very favorable interaction for the subsequent oxidation of CO, supporting our experimental observation of the low-temperature CO oxidation activity of the supported Au₂₂(L⁸)₆ nanoclusters.

In conclusion, we have deposited the atomically precise, monodispersed Au₂₅(L⁸)₆ nanoclusters (L⁸ = 1,8-bis(diphenylphosphino)octane) with in situ Au sites intactly onto reducible and nonreducible oxide supports (TiO₂, CeO₂, and Al₂O₃). A variety of in situ approaches including EXAFS, atomically resolved HAADF-STEM, and IR spectroscopy consistently demonstrate that the supported Au₂₅(L⁸)₆ nanoclusters are stable to heating in vacuum or dilute O₂ without favorable interaction for the subsequent oxidation of CO, and TiO₂.(PDF)

■ ASSOCIATED CONTENT

 Supporting Information

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Experimental details. Figures showing views, a UV−vis spectrum, an MS pattern, TGA, the Au₂₅(L⁸)₆ nanoclusters; in situ HAADF-STEM images and IR back-

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