NANO LETTERS
Letter
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Diphosphine-Protected Au_{22} Nanoclusters on Oxide Supports Are Active for Gas-Phase Catalysis without Ligand Removal

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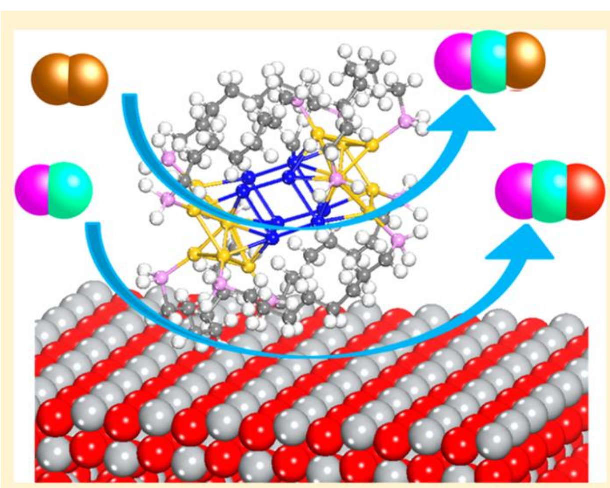

DOI: 10.1021/acs.nanolett.6b03221
Nano Lett. 2016, 16, 6560−6567

Shridevi Bhat
22/07/2017

Background

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Controlling Gold Nanoclusters by Diphospine Ligands

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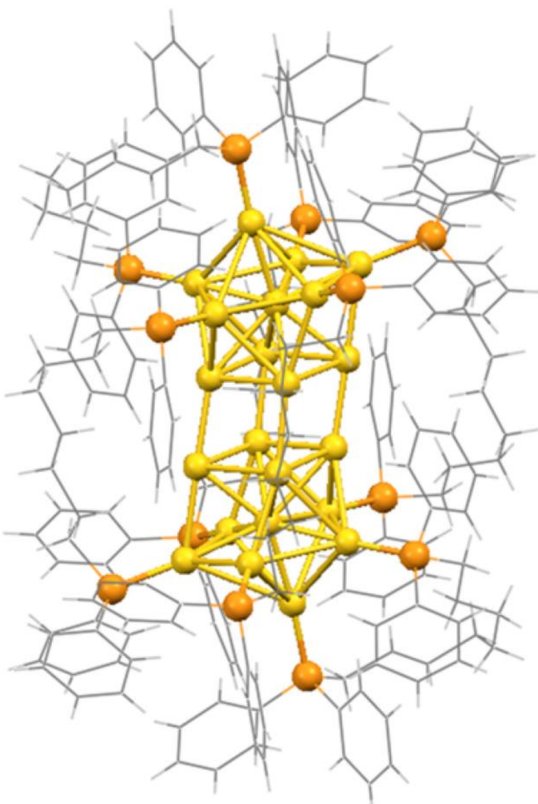
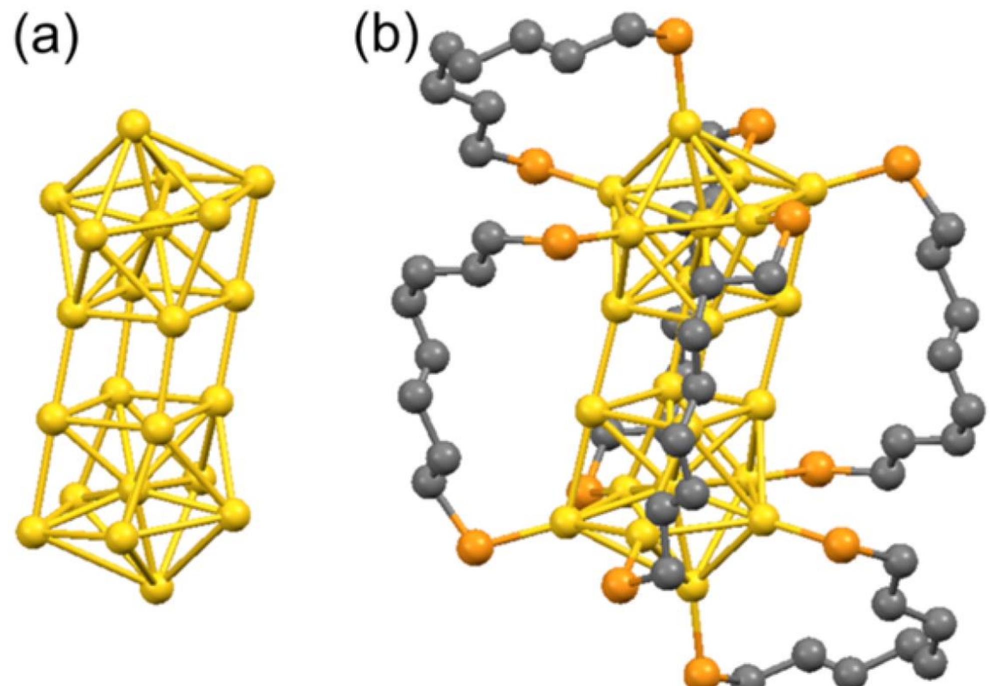
Total structure of the $Au_{22}(L^8)_6$ cluster



Core structure of the $Au_{22}(L^8)_6$ cluster



L = 1,8-bis(diphenylphosphino) octane

Color labels: yellow = Au; orange = P; gray = C

dx.doi.org/10.1021/ja411061e
J. Am. Chem. Soc. 2014, 136, 92–95

Background

Electronic and optical properties of the Au_{22}[1,8-bis(diphenylphosphino) octane]$_6$ nanoclusters disclosed by DFT and TD-DFT calculations

Francesco Muniz-Miranda[1] · Davide Presti[1] · Maria Cristina Menziani[1] ·
Alfonso Pedone[1]

Furthermore, the cluster also possesses the unique peculiarity of having 8 Au atoms on the surface of the metal core that are not engaged in covalent bonds with the organic ligands. These atoms could possibly be exploited in catalysis, and we found that their almost vanishing partial charges differ considerably from those of nearby atoms (which are markedly negative).

Theor Chem Acc (2016) 135:5
DOI 10.1007/s00214-015-1764-x

In this paper

- The catalytic behaviour of a $Au_{22}(L^8)_6$ cluster with in situ uncoordinated Au sites supported on TiO_2, CeO_2, and Al_2O_3 is explored.

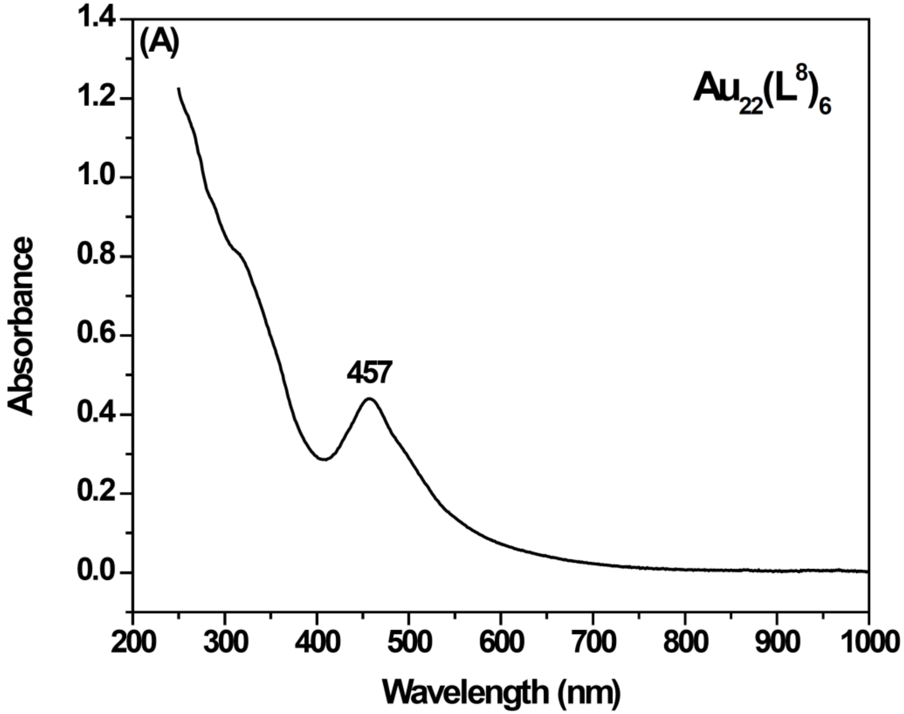
- Stability of the supported Au_{22} nanoclusters was probed structurally by in situ extended X-ray absorption fine structure (EXAFS) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and their ability to adsorb and oxidize CO was investigated by IR absorption spectroscopy and a temperature-programmed flow reaction.

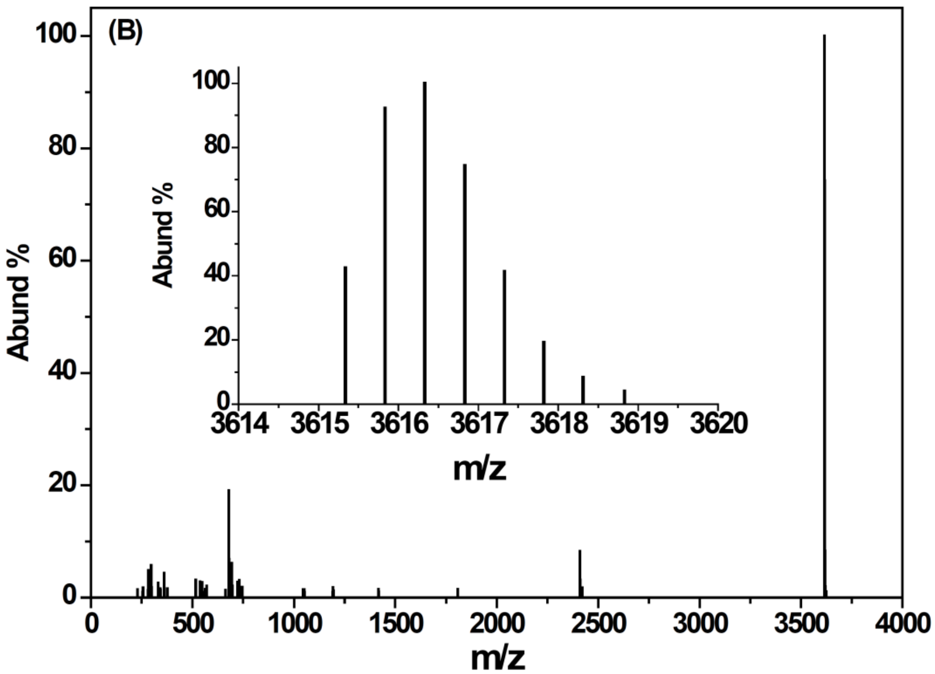
- Low-temperature CO oxidation activity was observed for the supported pristine $Au_{22}(L^8)_6$ nanoclusters without ligand removal.

- Density functional theory (DFT) calculations confirmed that the eight uncoordinated Au sites in the intact $Au_{22}(L^8)_6$ nanoclusters can chemisorb both CO and O_2.

- 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.

Synthesis and Characterization

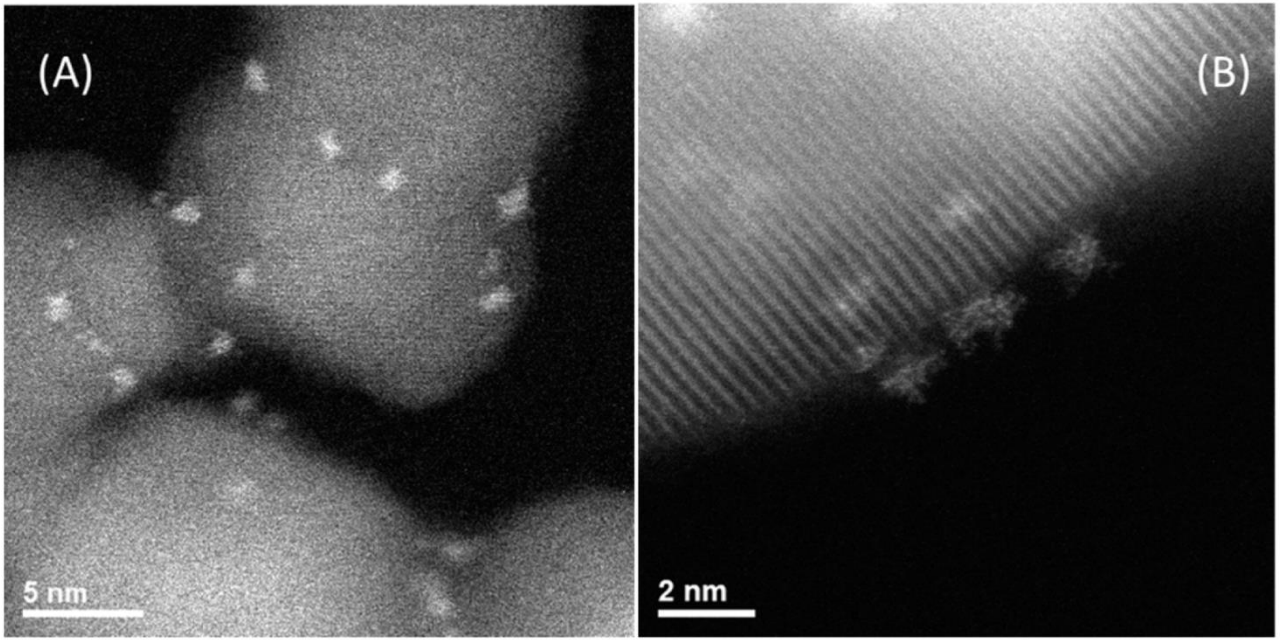




(A) UV-Vis spectrum of $Au_{22}(L^8)_6$ measured in CH_2Cl_2; (B) MS pattern for $Au_{22}(L^8)_6$, insert shows the isotopic pattern for $[Au_{22}(L^8)_6 + 4H]^{3+}$.

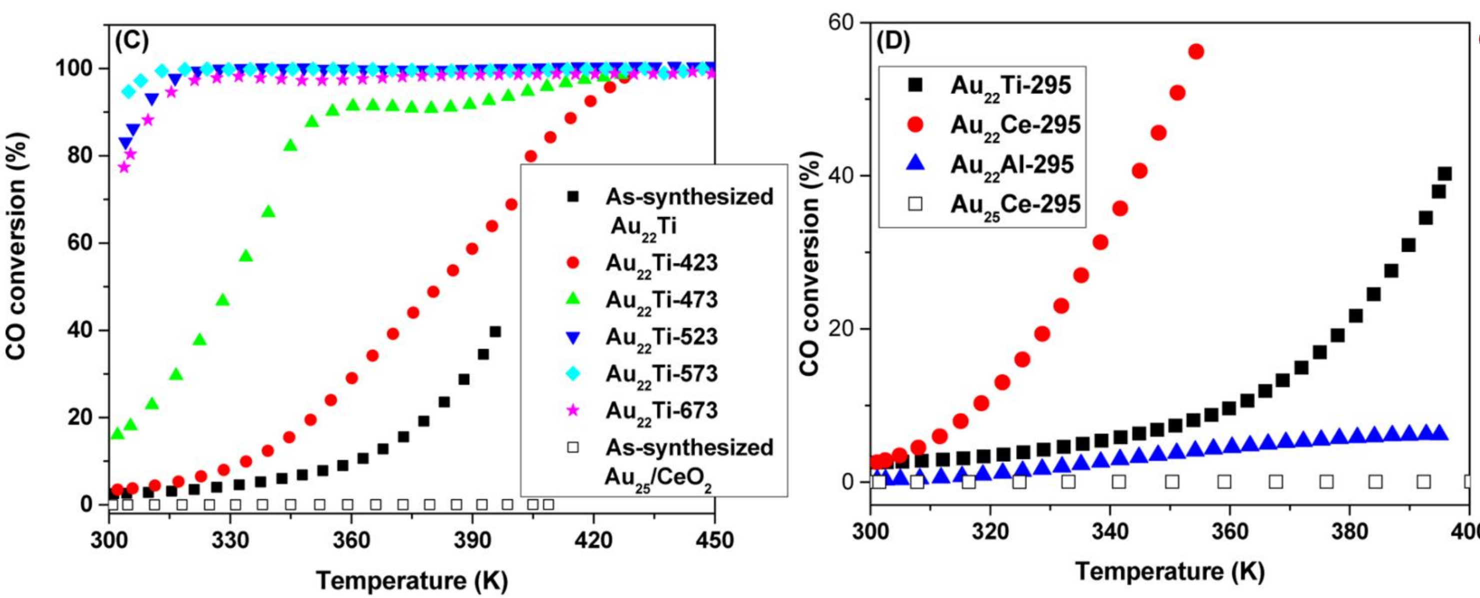
Results and Discussion

Observation of CO oxidation over supported $Au_{22}(L^8)_6$



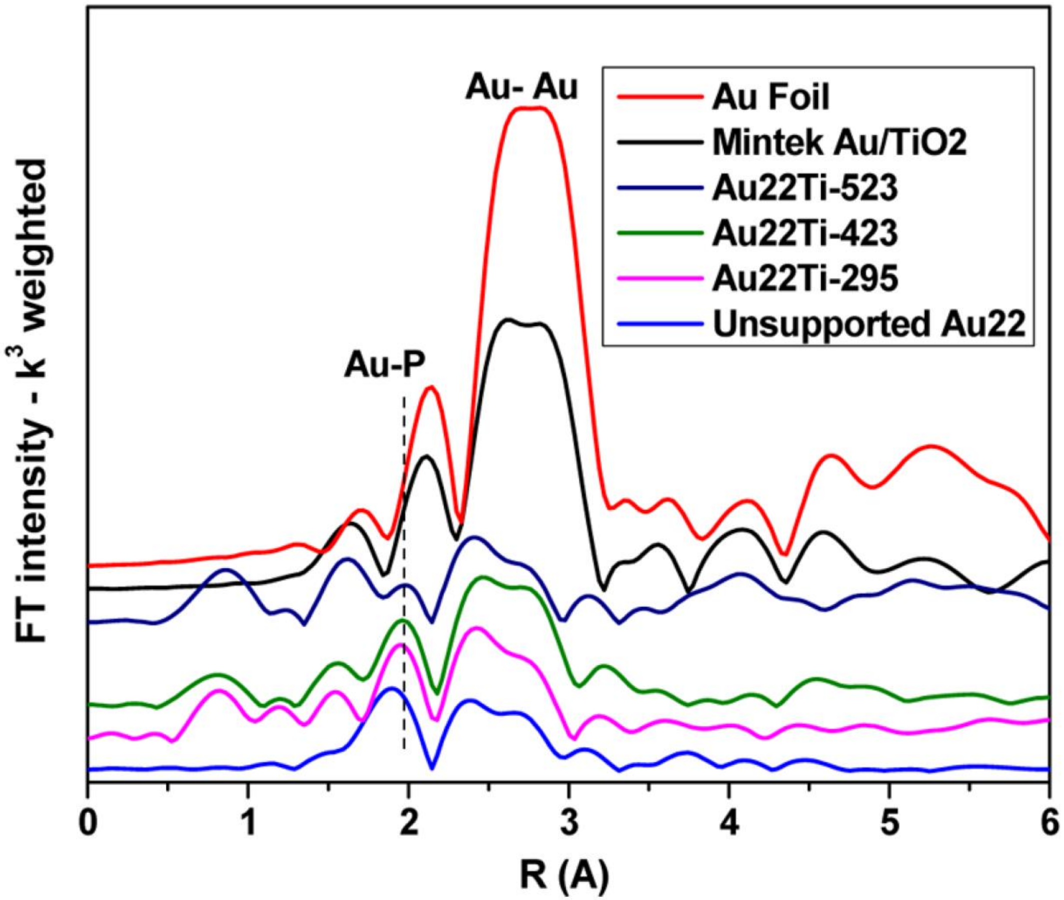
(A,B) HAADF-STEM images of as-synthesized $Au_{22}(L^8)_6$-TiO_2 in different magnifications.

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.
TOF for a typical Au-TiO2 nanocatalyst (0.023 s^{-1}).



CO oxidation light-off curves for different temperature treated $Au_{22}(L^8)_6$-TiO_2 samples (C) and the as-synthesized $Au_{22}(L^8)_6$ supported on TiO_2, CeO_2, and Al_2O_3 (D). The light-off curve from as-synthesized $Au_{25}(SR)_{18}$-CeO_2 is also included in the two figures for comparison.

State of the L^8 ligands in the supported $Au_{22}(L^8)_6$



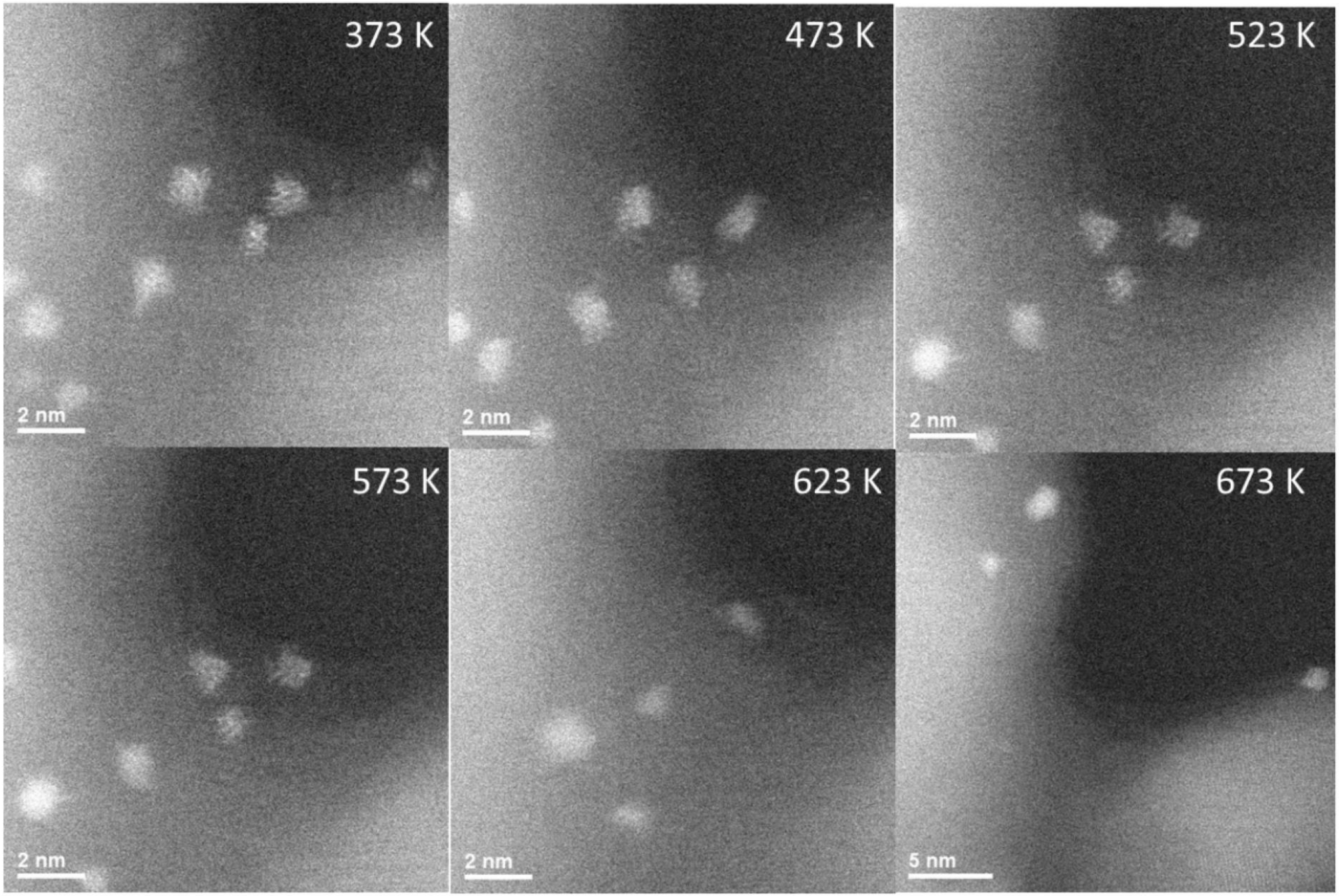
Whether the Au_{22} nanoclusters are intact on TiO_2?

The Au-P distance for unsupported Au_{22} is 2.28 Å and coordination number is 0.5, which remain unchanged for supported cluster. This suggests that the Au nanoclusters dispersed on the TiO2 surface are similarly coordinated with the diphosphine ligands as in the unsupported case. The core structure of supported cluster also largely resembles that of unsupported cluster as indicated by Au-Au feature.

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.

Results and Discussion

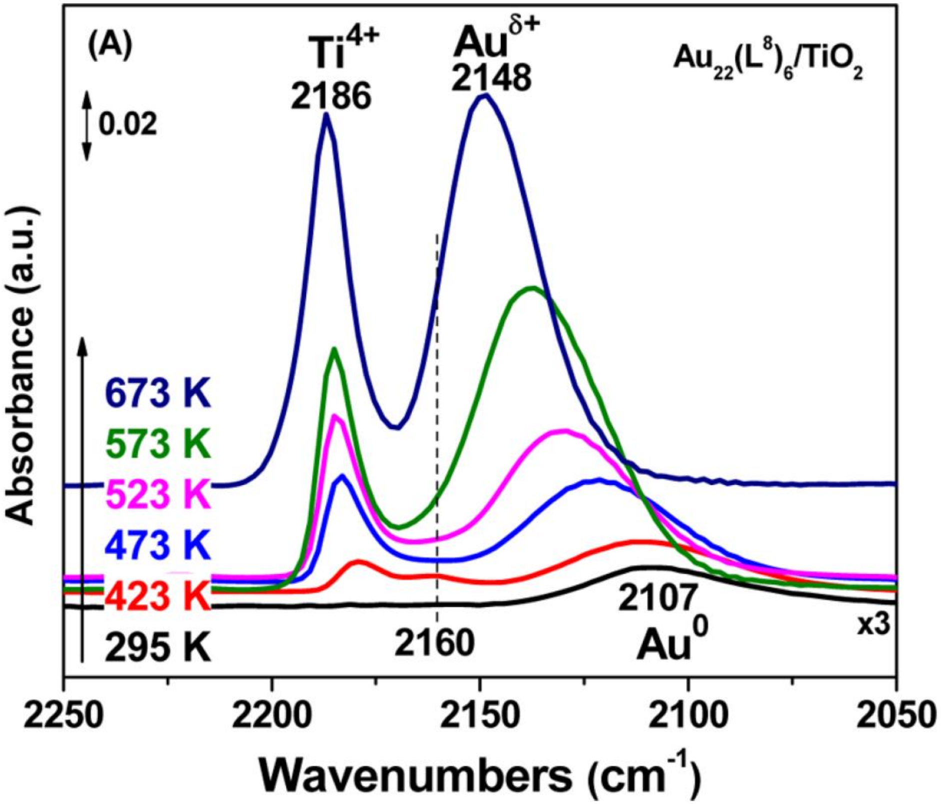
State of the L^8 ligands in the supported $Au_{22}(L^8)_6$

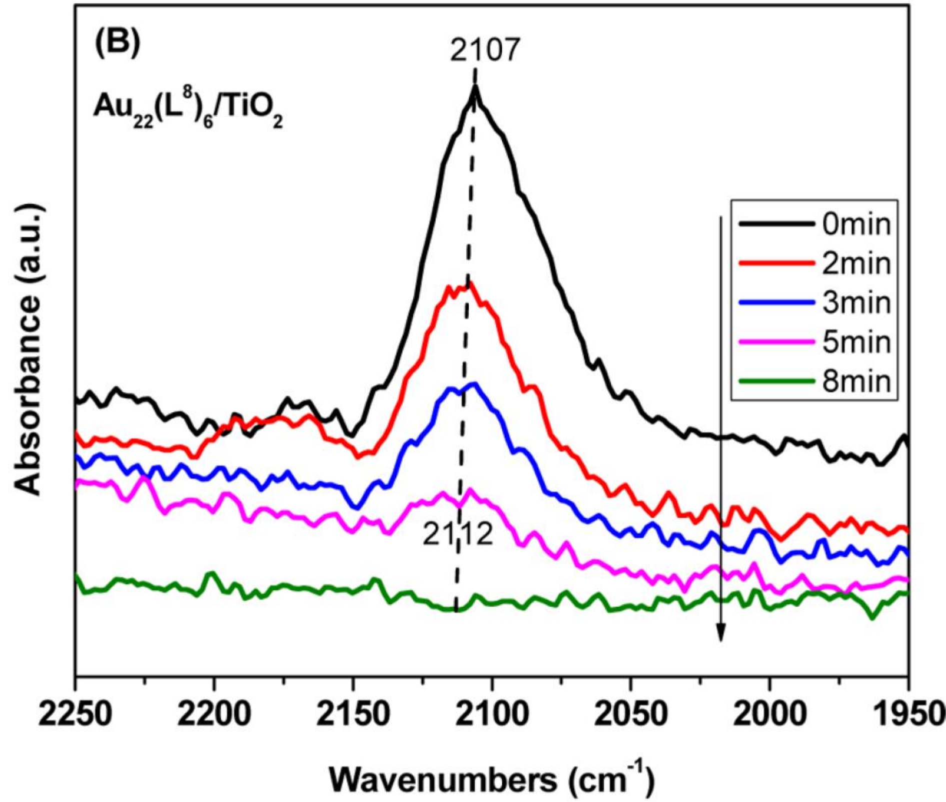


In situ HAADF-STEM images of $Au_{22}(L^8)_6$ /TiO_2 at high magnification collected during heat treatment at different temperatures in 300 Torr O_2.

Results and Discussion

Nature of the Au sites on the $Au_{22}(L^8)_6$ cluster surface

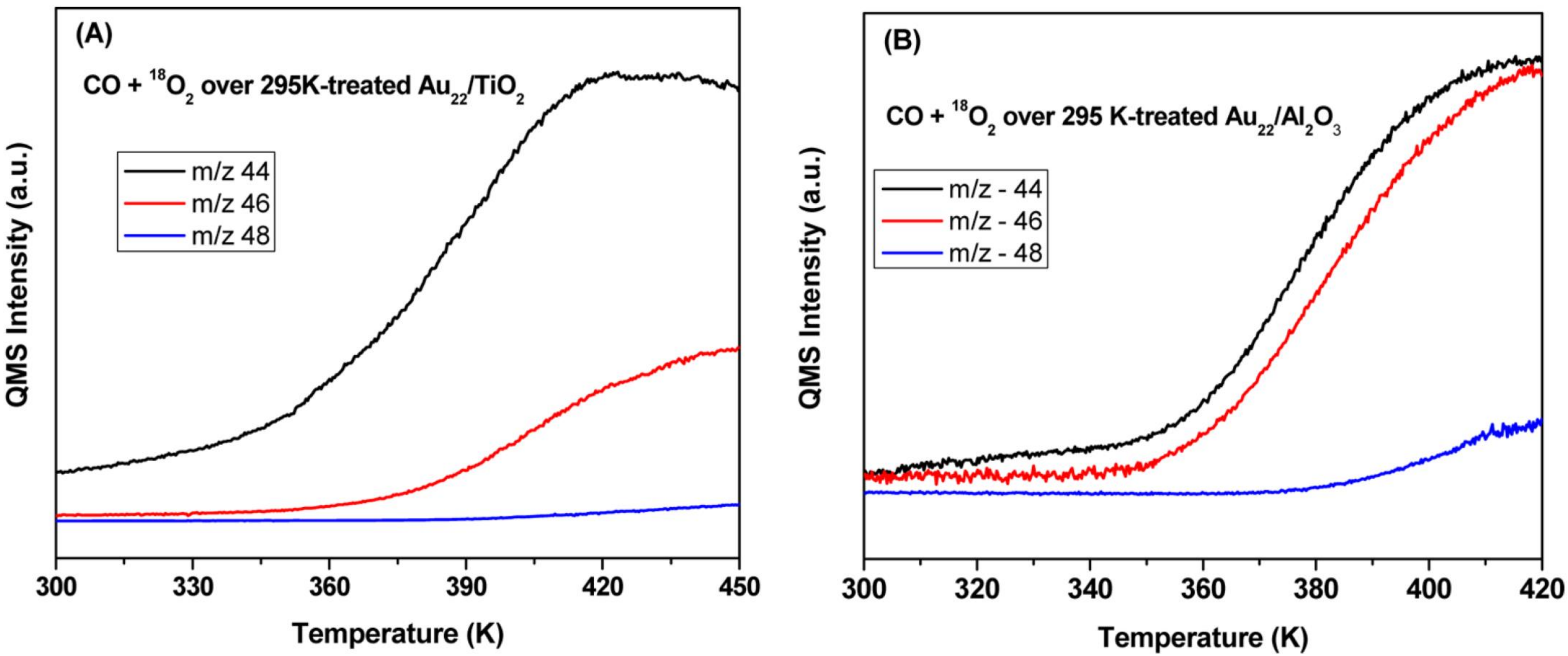




(A) IR spectra of CO adsorption at room temperature on $Au_{22}(L^8)_6$-TiO_2 pretreated in O_2 at different temperatures. (B) IR spectra from CO desorption at room temperature in flowing O_2 on as-synthesized $Au_{22}(L^8)_6$-TiO_2.

Results and Discussion

Reaction mechanism



QMS profiles of CO_2 isotopomers evolved during CO + $^{18}O_2$ over as-synthesized $Au_{22}(L^8)_6$-TiO_2 (A) and $Au_{22}(L^8)_6$-Al_2O_3 (B).

Mars-van Krevelen (MvK) mechanism

CO is reacts with $Ti^{16}O_2$ lattice oxygen to form CO_2

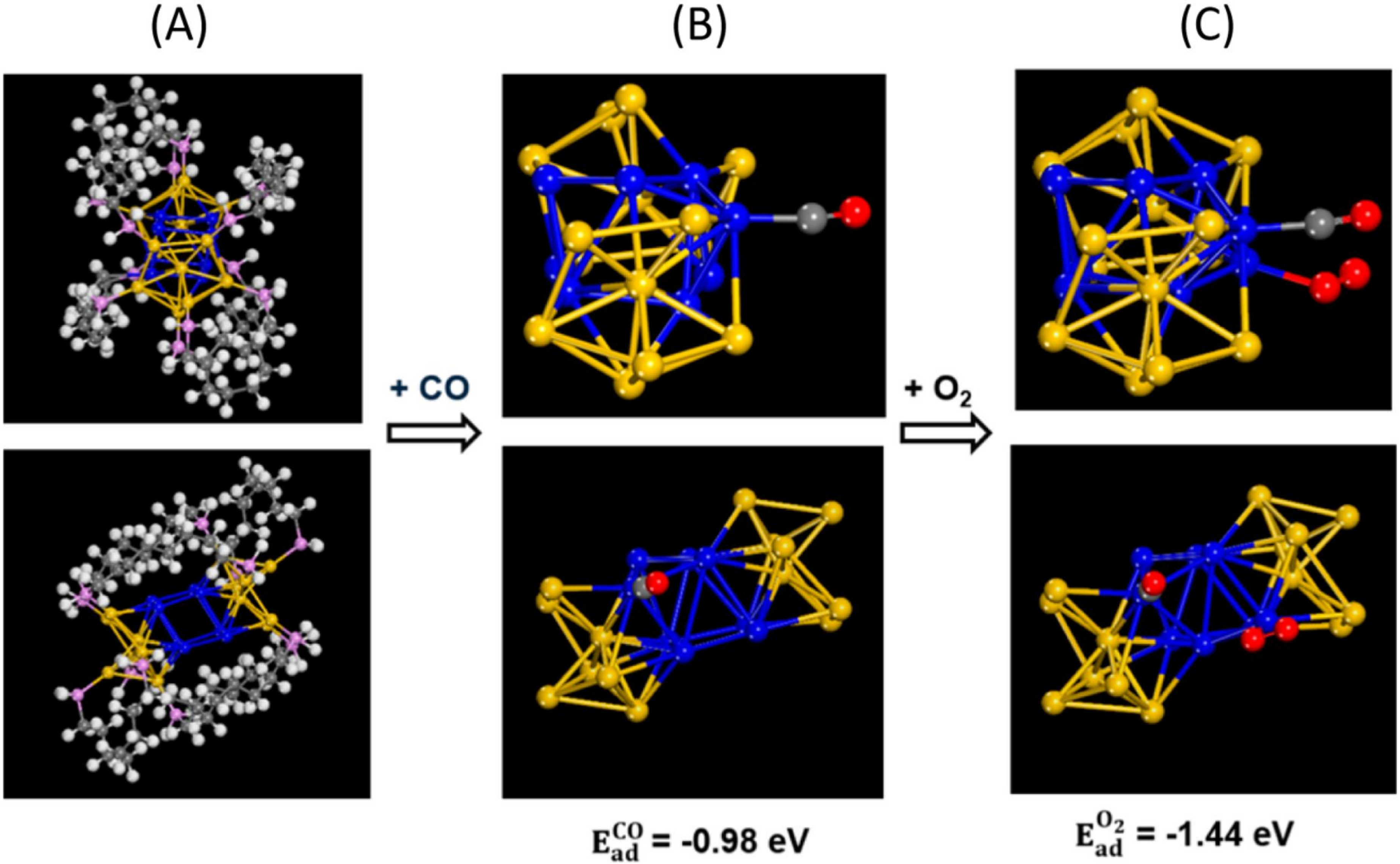
The growth of $C^{16}O^{18}O$ at higher temperature is due to the reaction of CO with lattice ^{18}O replenished by the gas phase $^{18}O_2$.

Langmuir-Hinshelwood (L-H) mechanism on the cus Au sites

Both CO and O_2 are activated and reacted.

Results and Discussion

Reaction mechanism



Front (upper panel) and side (lower panel) views of the $Au_{22}(L^8)_6$ nanocluster (A), CO adsorption (B), and O_2 coadsorption (C). Ligands are omitted for clarity in panels b and c. Color labels - cus Au, blue; other Au, yellow; C, gray; H, white; P, pink; O, red.

Conclusion

- They have deposited the atomically precise, monodispersed $Au_{22}(L^8)_6$ nanoclusters (L^8 = 1,8-bis-(diphenylphosphino) octane) with in situ cus Au sites intactly onto reducible and nonreducible oxide supports (TiO_2, CeO_2, and Al_2O_3).

- The supported $Au_{22}(L^8)_6$ nanoclusters readily exhibit CO adsorption and CO oxidation activity in the as-deposited state without ligand removal.

- DFT models for the unsupported $Au_{22}(L^8)_6$ nanocluster suggest that, the fully ligated Au_{22} nanoclusters present coordinatively unsaturated, neutral Au atoms that are available for bonding to CO and catalysing its oxidation.

- CO oxidation activity is enhanced on the more reducible CeO_2 support than TiO_2 and Al_2O_3 and isotope labeling demonstrates that the primary low-temperature pathway is through a Mars--van Krevelen route utilizing the lattice oxygen of the oxide support.