CO Oxidation on TiO_2(110) Supported Subnanometer Gold Clusters: Size and Shape Effects

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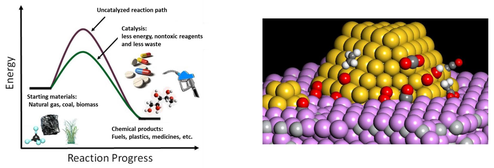
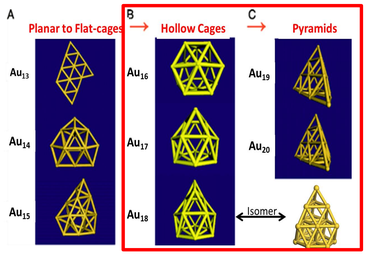
INTRODUCTION

1. Catalyst can effectively reduce the energy cost and the formation of by-product while increase yield of target product. It is involved in ~90% of commercially produced chemical products.



2. Gold nanoparticles (especially deposited onto metal oxide supports, such as TiO_2) as a highly active catalyst have been extensively studied; are active to numerous chemical reactions such as CO oxidation, propylene epoxidation and the water-gas shift, etc. CO oxidation is commonly used as a probe to scale their activity.
3. The structures of gold clusters vary with their size.: planar→ flat-cages→hollow cages →pyramidal structures.



4. To improve catalytic properties, first we need to understand the origins of high catalytic activity of Au/oxide catalysts. Systematic studies of catalytic activity of sub-nanometer Au clusters, such as $Au_{1\text{-}4,\ 7}$ and $Au_{16\text{-}20}$, can address some critical questions:

- ❖ Reaction mechanism: how does the reaction proceed on Au/TiO_2?
- ❖ Effects of support: What role does the TiO_2 support play during CO oxidation?
- ❖ Size and shape dependence: what kind of clusters is more active, e.g. smaller or larger clusters? hollow-cage or pyramidal clusters?

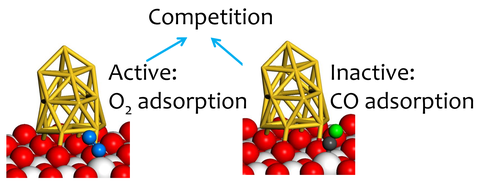
COMPUTATIONAL DETAILS

Simulation of CO Oxidation:

For geometric optimization and searching the transition state, Dmol3 package is used. Details: GGA in PBE form. The real-space global cutoff radius is set to be 4.0 angstrom. Double numerical basis with d-polarization (DND) and semi-core pseudo potential are used to treat atomic orbitals and core electrons, respectively. The transition state search scheme is based on a combination of LST/QST methods. To avoid the interaction of neighbor clusters in periodic boundary condition, two large supercells (6×3 and 5×3) are used for the simulations of CO oxidation on the supported pyramidal Au clusters and cage-like Au clusters, respectively.

Born-Oppenheimer molecular dynamics is used to simulate the soft-landing process of Au clusters onto TiO_2(110) surface and CO oxidation at the Au-TiO_2 interface

Reaction Kinetics:

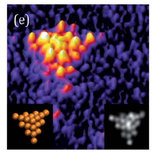


$$R = \frac{k_2^+ k_1^+ K_{CO}^* K_{O_2}^\ddagger [1 + K_{O_2}^\ddagger P_{O_2} + \boldsymbol{K_{CO}^\ddagger P_{CO}}]}{(k_1^- + k_2^+)[1 + K_{CO}^* P_{CO} + K_{O_2}^* P_{O_2}]} P_{CO} P_{O_2} \theta_\ddagger{}^2$$

RESULTS AND DISCUSSION

1. Hollow-cage, pyramidal $Au_{18\text{-}20}$ on substrates

(1) Pyramidal Structure ($Au_{20\pm1}$): experimentally imaged on the amorphous carbon substrate



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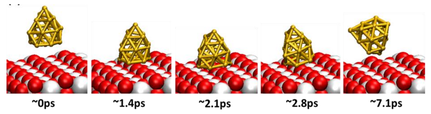
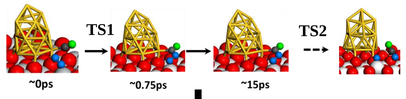
(2) Hollow-cage Au_{18}: sustain from collision with TiO_2(110) surface at initial speed 200 m/s.



➢ Upon deposited onto substrates, Au clusters can exhibit hollow-cage and pyramidal structures. So it is reasonable to use them as models to study catalytic properties of Au/TiO_2 systems

2. DPS mechanism on $Au_{16\text{-}20}$ on TiO_2

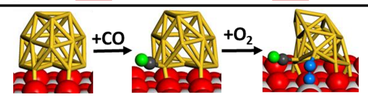
(1) OCOO* intermediate formation on $Au_{18\text{-cage}}/TiO_2$: MD simulation at 125K



Langmuir-Hinshelwood (L-H) Mechanism at dual perimeter sites (simplified as DPS mechanism)

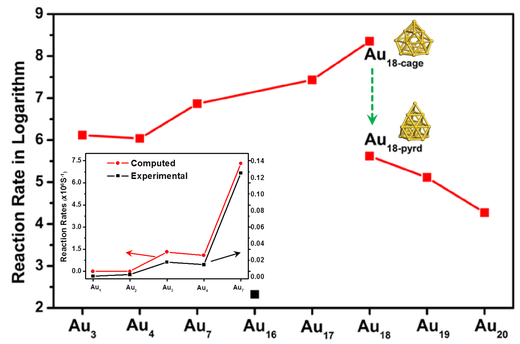
(2) Reaction-pathway study

	Au_n	E_a^{TS1}	E_a^{TS2}	E_{ad}^{CO}	$E_{ad}^{CO^+}$	$E_{ad}^{O_2}$	O_2/CO	$\theta_{O_2}^\ddagger$	R_1/S^{-1}
Cage	Au_{16}	0.62	0.31	-0.56	-0.42	-0.69	1.64	9.889×10^{-1}	2.096×10^2
	Au_{17}	0.05	0.24	-0.45	-0.44	-0.14	0.32	4.659×10^{-5}	2.725×10^7
	$Au_{18\text{-cage}}$	0.10	0.26	-0.41	-0.40	-0.30	**0.75**	$1.629 \times \mathbf{10^{-2}}$	$\mathbf{2.248 \times 10^8}$
Pyramid	$Au_{18\text{-pyrd}}$	0.10	0.29	-0.74	-0.43	-0.07	0.16	3.275×10^{-6}	4.141×10^5
	Au_{19}	0.12	0.28	-0.75	-0.42	-0.06	0.14	3.275×10^{-6}	1.289×10^5
	Au_{20}	0.13	0.28	-0.67	-0.44	-0.02	0.05	4.710×10^{-7}	1.864×10^4



➢ Comparable reaction barriers (0.24 - 0.29 eV)
➢ Distinctive O_2/CO ratio due to different O_2 adsorption strength

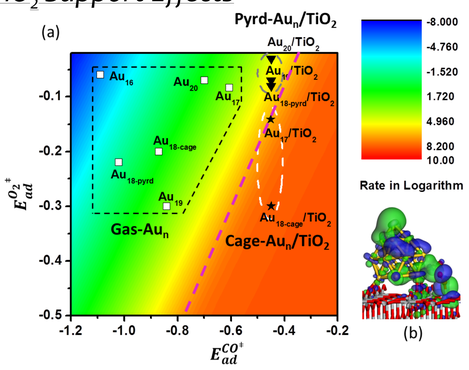
3. Size and Shape Effect



Reaction rates v.s. Size of Au_n: Experimental values from *J. Am. Chem. Soc*, **2004**, *126*, 5682

➢ The trend of computed reaction rates is in good agreement with experimental results.
➢ Catalytic activities increase with the size *n* up to 18
➢ Hollow-cage Au_n is much more active than pyramidal Au_n

4. TiO_2 Support Effects



Contour map of reaction rates v.s. CO and O_2 adsorption energy

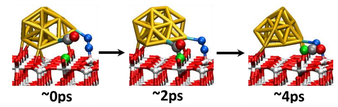
➢ To reach the critical line (purple line), a critical adsorption-energy ratio of O_2 to CO (O_2/CO ratio) is required.
➢ Weaker adsorption of CO on the TiO_2 support decreases the critical O_2/CO ratio for reaching the critical line, thus resulting in significantly enhanced reaction rates.

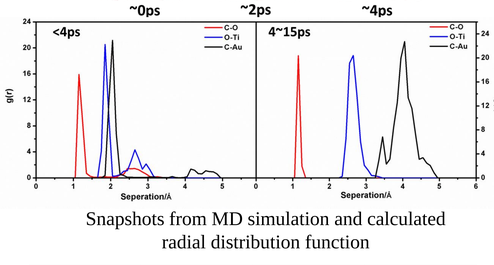
5. Generation of Oxygen vacancy

(1) Au_{16} soft-lands onto TiO_2 (110) surface:

✓ Attach onto the surface
✓ Structure deformation induced → More flexible

(2) CO Reacts with the surface lattice oxygen atom on Au_{16}/TiO_2: MD simulation at 125K





Snapshots from MD simulation and calculated radial distribution function

	O_2 adsorption	M-K Mechanism		L-H Mechanism	
		TS1	TS2	TS1	TS2
Au_{16}	-0.70	0.18	0.35	0.62	0.31
$Au_{18\text{-cage}}$	-0.30	0.24	0.41	0.10	0.26

Mars-van Krevelen (M-K) Mechanism v.s. L-H Mechanism

✓ Flexible Au_{16}: CO tends to react with lattice oxygen atoms instead of O_2 molecules
✓ Robust Au_{18}: L-H mechanism is more promising due to the readily formation of OCOO* intermediates

Reference

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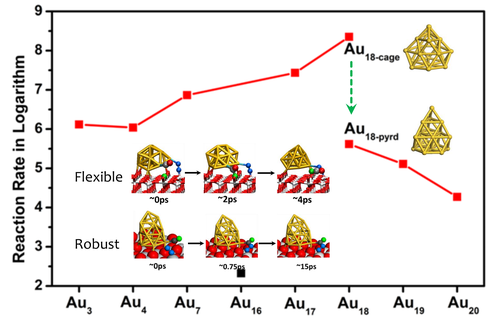
SUMMARY OF MAIN FINDINGS

1. Size effect: catalytic activities of Aun/TiO_2 systems increase with the size n up to 18. However, further increasing of the size reduces the activities for CO oxidation.
2. Shape effect: supported hollow-cage Au_{18} exhibits significantly high catalytic activity due to the enhanced O_2 adsorption by *d*-π interaction . However, the pyramidal isomer entails much lower reaction rates. Pyramidal gold clusters (on TiO_2 support) are expected to be less active.
3. For flexible Au_{16}: the strong binding of O_2 with the low-coordinated Au atom inhibits its activity, but it can promote CO to react with lattice oxygen atoms to generate oxygen vacancy.
   For robust Au_{18}: Langmuir-Hinshelwood mechanism is favorable due to the formation of OCOO* intermediates



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