An Atomic-Level Strategy for Unraveling Gold Nanocatalysis from the Perspective of $Au_n(SR)_m$ Nanoclusters

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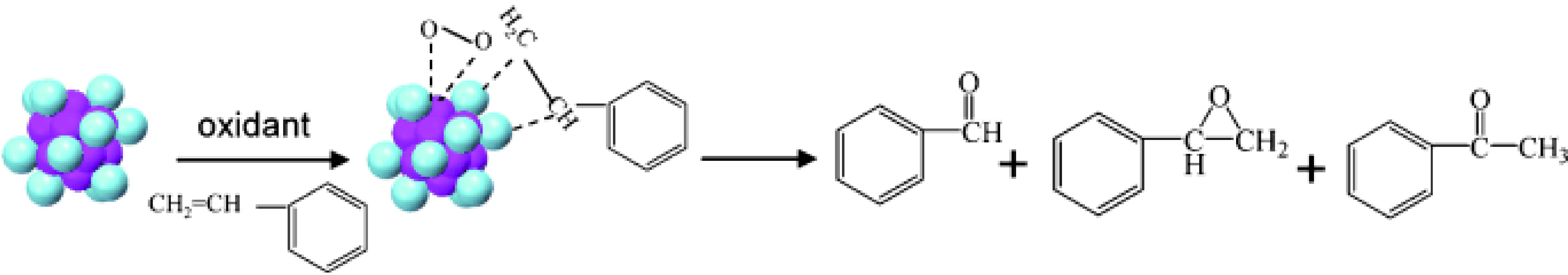
Introduction

- Gold nanoparticles are found to exhibit catalytic activity in many chemical processes
- Due to the polydispersity the structure-catalytic activity relationships are not fully understood
- Identifying catalytically active species is difficult if the surface structure is unknown
- The 2D and 3D model gold catalysts are better defined but the results in UHV are deviated from realistic conditions. So they can not be directly transferable to real world catalytic systems
- Due to structural polydispersity and heterogeneity of conventional systems the results are an average ensemble only
- Recently atomically mono disperse $Au_n(SR)_m$ are found to show catalytic properties
- Since these nanoclusters are well defined and their structures start to be solved, there are chances for studies to correlate structure-catalytic activity

- There are numerous studies on ligand removed Au_n clusters and gas phase deposited Au_n cluster for CO and alkene oxidations
- By understanding the structure and electronic properties, this group designed $Au_{25}(SR)_{18}$ as catalyst for hydrogenation of ketones

In this paper….

- Au_{25}, Au_{38} and Au_{144} clusters capped with phenyl ethane thiolate were prepared using wet-chemistry approach
- Size effect on selective oxidation of styrene is studied
- Effect of oxidants (TBHP, O_2) and supports (SiO_2 and HAP) is studied



Experimental Section

Preparation of $Au_{25}(SCH_2CH_2Ph)_{18}$:

$$HAuCl_4.3H_2O + PhCH_2CH_2SH + NaBH_4 \xrightarrow{\text{one day reaction}} \text{ethanol, followed by extraction with acetonitrile}$$

in toluene

Preparation of $Au_{38}(SCH_2CH_2Ph)_{24}$:

$$\underset{\text{acetone}}{HAuCl_4\cdot 3H_2O + GSH} \xrightarrow[NaBH_4]{0^oC} \underset{\text{black}}{Au_n(SG)_m}$$

$$\underset{200\text{–}300\text{ mg}}{Au_n(SG)_m} + \underset{0.3\text{ mL}}{\text{ethanol}} + \underset{2\text{ mL}}{\text{toluene}} + \underset{(2\text{ mL})}{PhCH_2CH_2SH} \xrightarrow[40\text{ hrs}]{353\text{ K}} \text{ethanol, followed by extraction with toluene}$$

Preparation of $Au_{144}(SCH_2CH_2Ph)_{60}$:

$$\underset{\text{in toluene}}{HAuCl_4.3H_2O} + PhCH_2CH_2SH + NaBH_4 \xrightarrow[\text{stirred overnight}]{0^oC} \text{residue}$$

$$20\text{ mg residue} + PhCH_2CH_2SH \xrightarrow[24\text{ hrs}]{80^oC} Au_{144}(SCH_2CH_2Ph)_{60} \text{ extracted with toluene}$$

➢ Preparation of supported $Au_n(SR)_m$ catalysts

SiO_2 + $Au_n(SR)_m$ in dichloromethane —One day stirring→

➢ The catalysts test

TBHP as an oxidant

$Au_n(SR)_m$ + styrene + TBHP + toluene —80ºC, 12 h→ NMR, GC-MS

$Au_n(SR)_m$	styrene	TBHP	toluene
1 wt% 100 mg	90 μL	0.5 mL	20 mL

O_2 as an oxidant

TBHP as an initiator and O_2 as an oxidant

TBHP = 7.2 μL

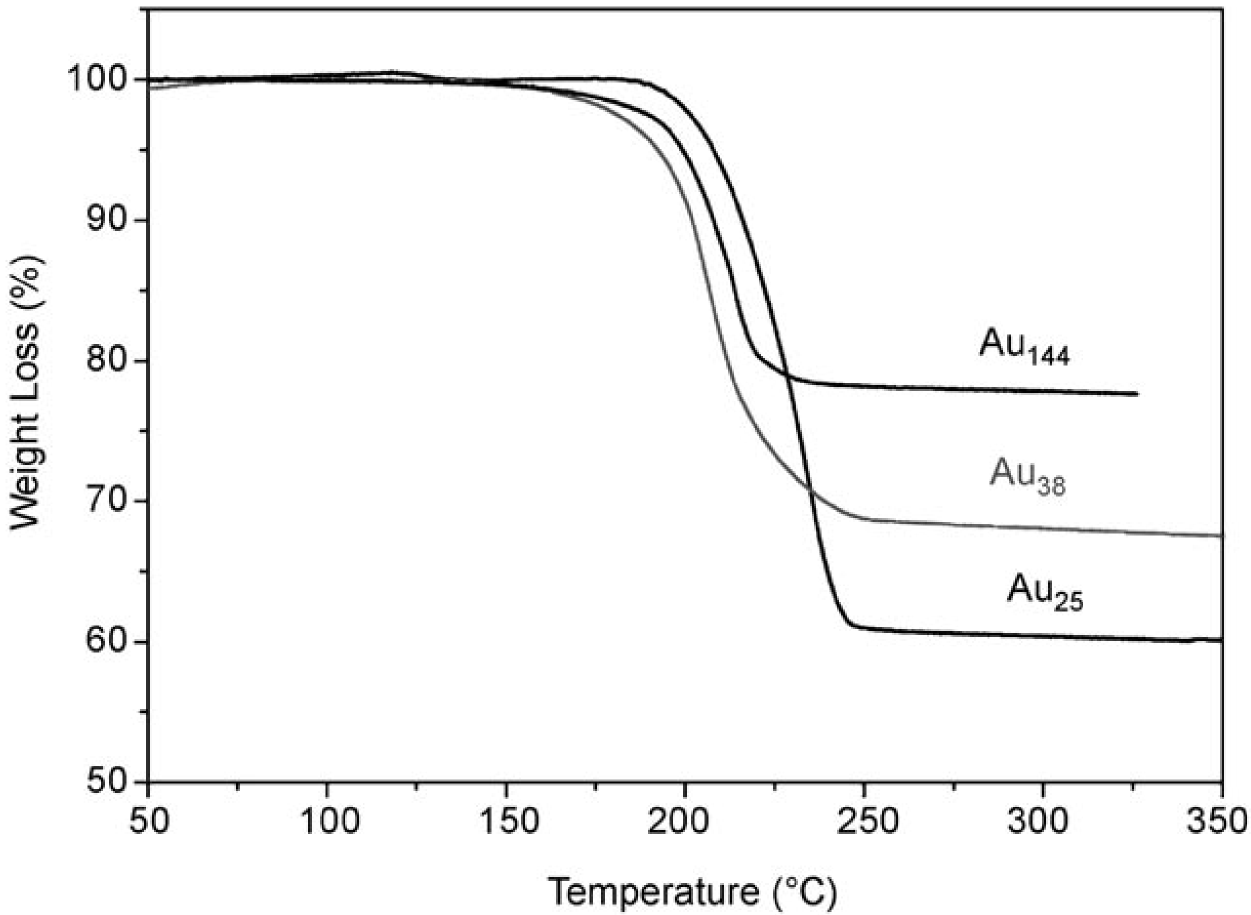


Figure 1. Thermogravimetric analysis (TGA) of $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{144}(SR)_{60}$ nanoclusters (R=CH_2CH_2Ph)

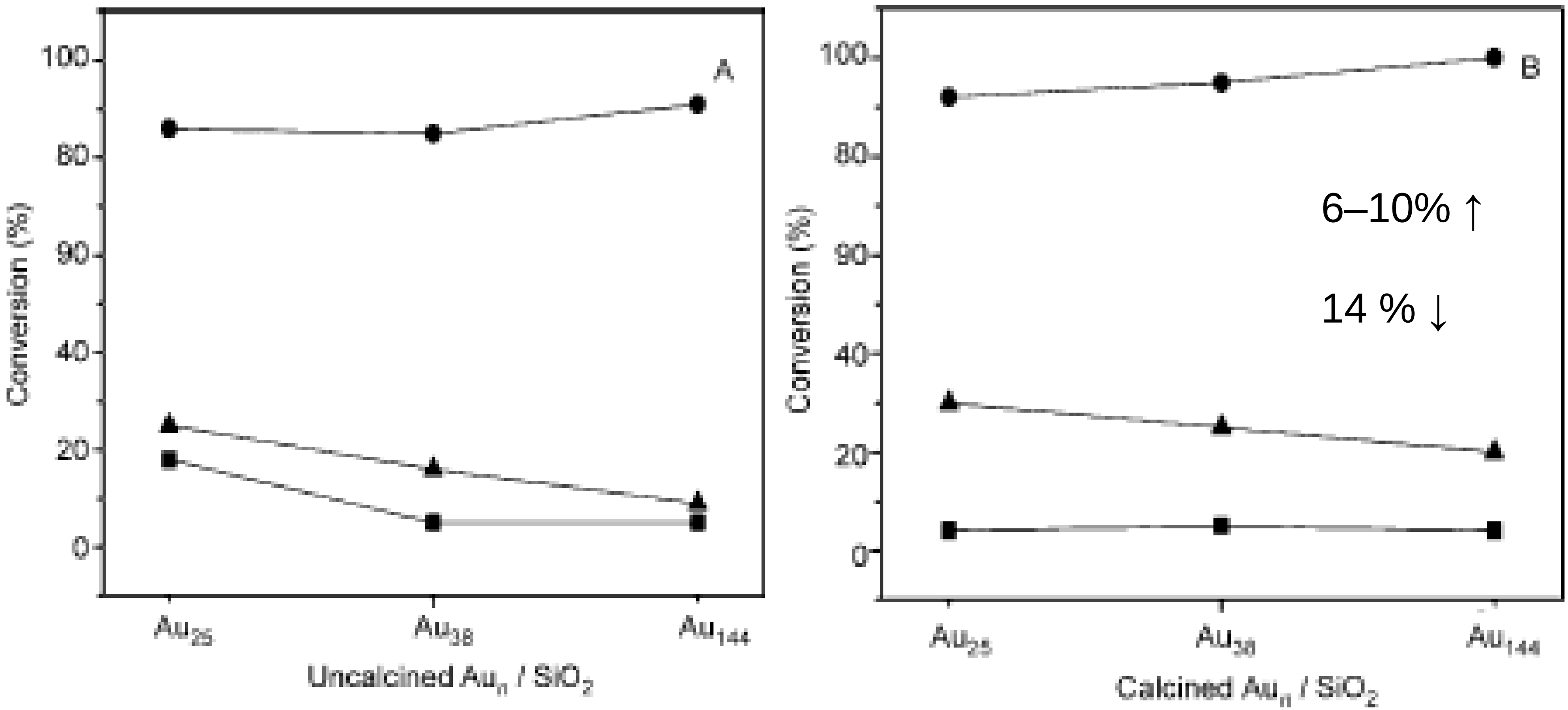


Figure 2. Catalytic activity of A) uncalcined $Au_n(SR)_m/SiO_2$ and B) at 200ºC calcined $Au_n(SR)_m/SiO_2$ catalysts for styrene oxidation. In each case, three systems are investigated: 1) TBHP as the oxidant ( ), 2) TBHP as an initiator and O_2 as the main oxidant ( ), and 3) O_2 as the sole oxidant ( ). Reaction conditions: 80ºC for 12 h in a toluene.

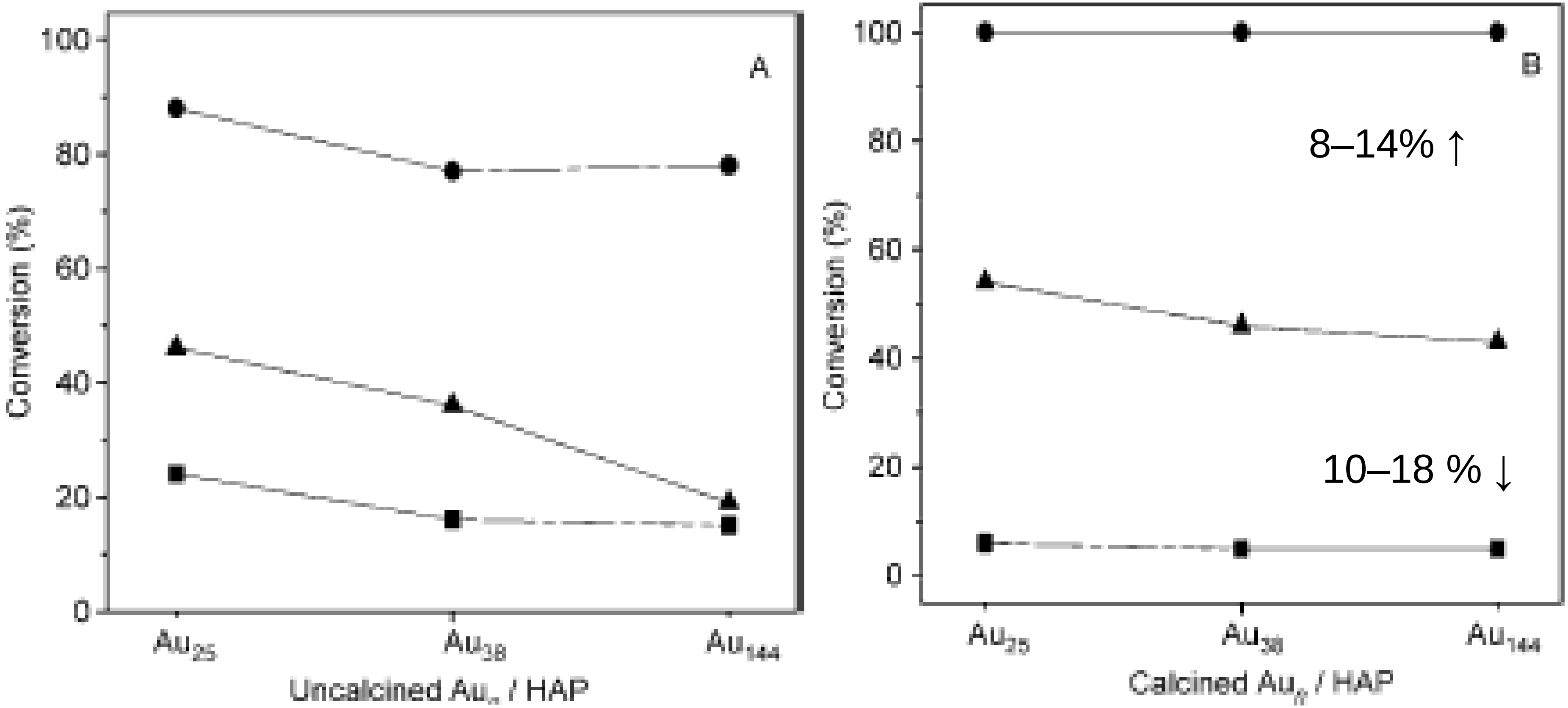


Figure 3. Catalytic activity of A) uncalcined $Au_n(SR)_m$/HAP and B) calcined $Au_n(SR)_m$/HAP catalysts for styrene oxidation. In each case, three oxidant systems are investigated: 1) TBHP as the oxidant ( ), 2) TBHP as an initiator and O_2 as the main oxidant ( ), and 3) O_2 as the sole oxidant ( ). Reaction conditions: 80ºC for 12 h in a toluene.

20 % ↑

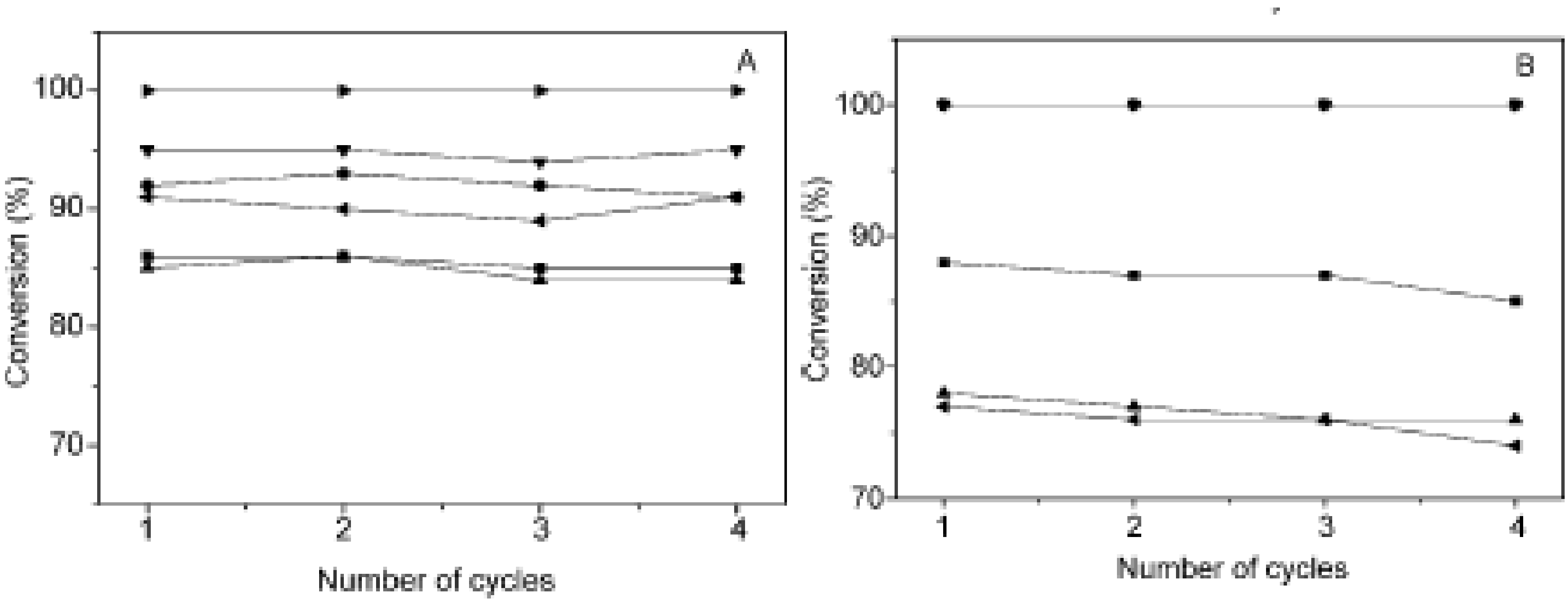


Figure 4. Recyclability of A) $Au_n(SR)_m/SiO_2$ and B) $Au_n(SR)_m$/HAP catalysts for styrene oxidation with TBHP as the oxidant system (=uncalcined supported Au_{25}, =calcined supported Au_{25}, =uncalcined supported Au_{38}, =calcined supported Au_{38}, ◄=uncalcined supported Au_{144}, and =calcined supported Au_{144}).

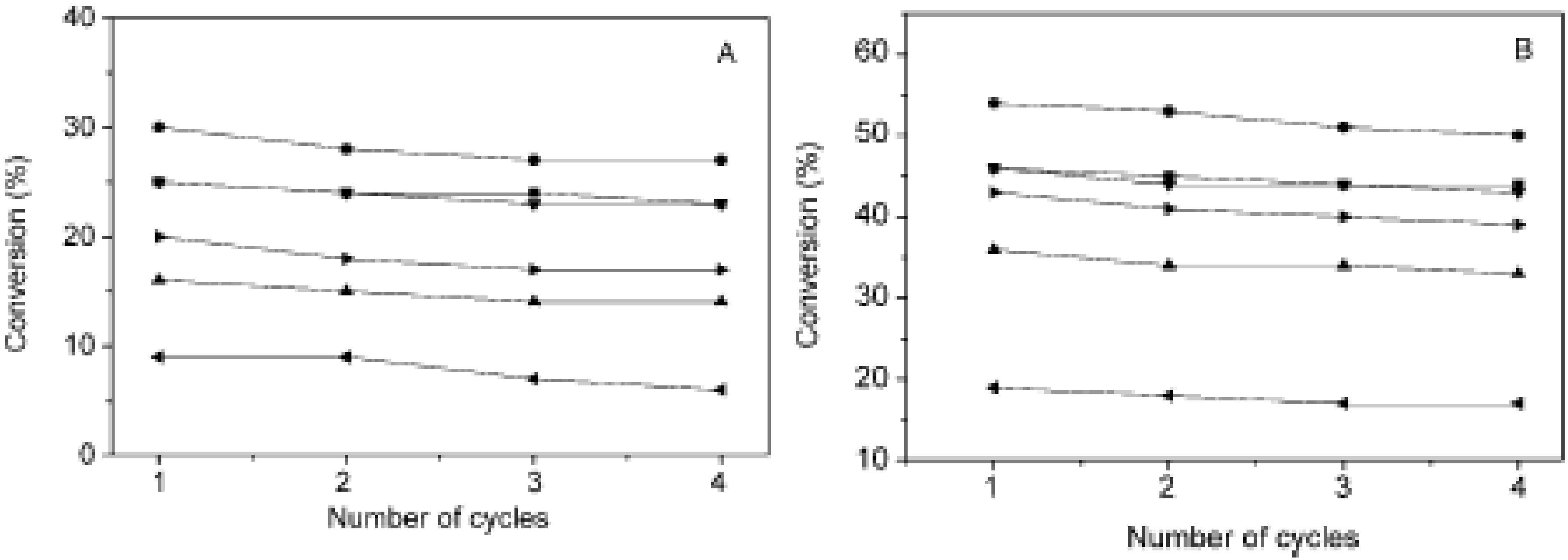


Figure 5. Recyclability of A) $Au_n(SR)_m/SiO_2$ and B) $Au_n(SR)_m$/HAP catalysts for styrene oxidation with TBHP as initiator and O_2 as the main oxidant system (=uncalcined supported Au_{25}, =calcined supported Au_{25}, =uncalcined supported Au_{38}, =calcined supported Au_{38}, ◄=uncalcined supported Au_{144}, and =calcined supported Au_{144}).

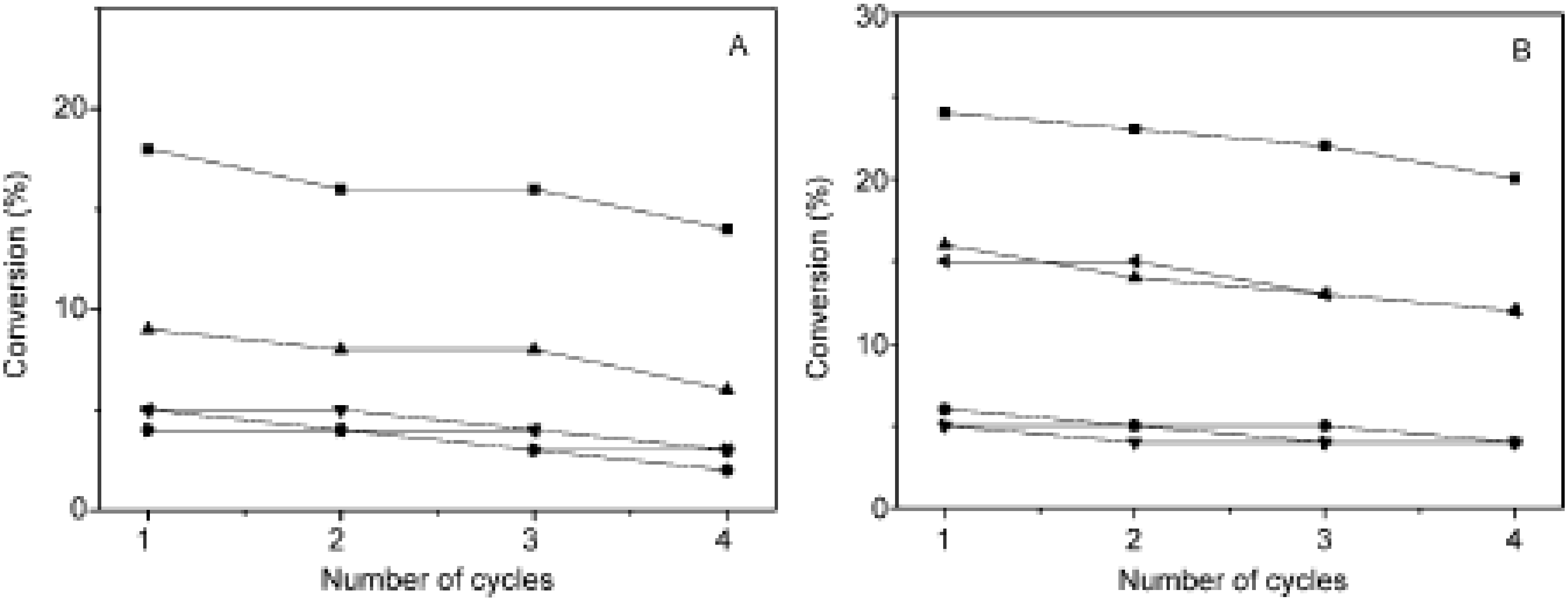


Figure 6. Recyclability of A) $Au_n(SR)_m/SiO_2$ and B) $Au_n(SR)_m$/HAP catalysts for styrene oxidation with O_2 as the sole oxidant system (=uncalcined supported Au_{25}, =calcined supported Au_{25}, =uncalcined supported Au_{38}, =calcined supported Au_{38}, ◀=uncalcined supported Au_{144}, and =calcined supported Au_{144}).

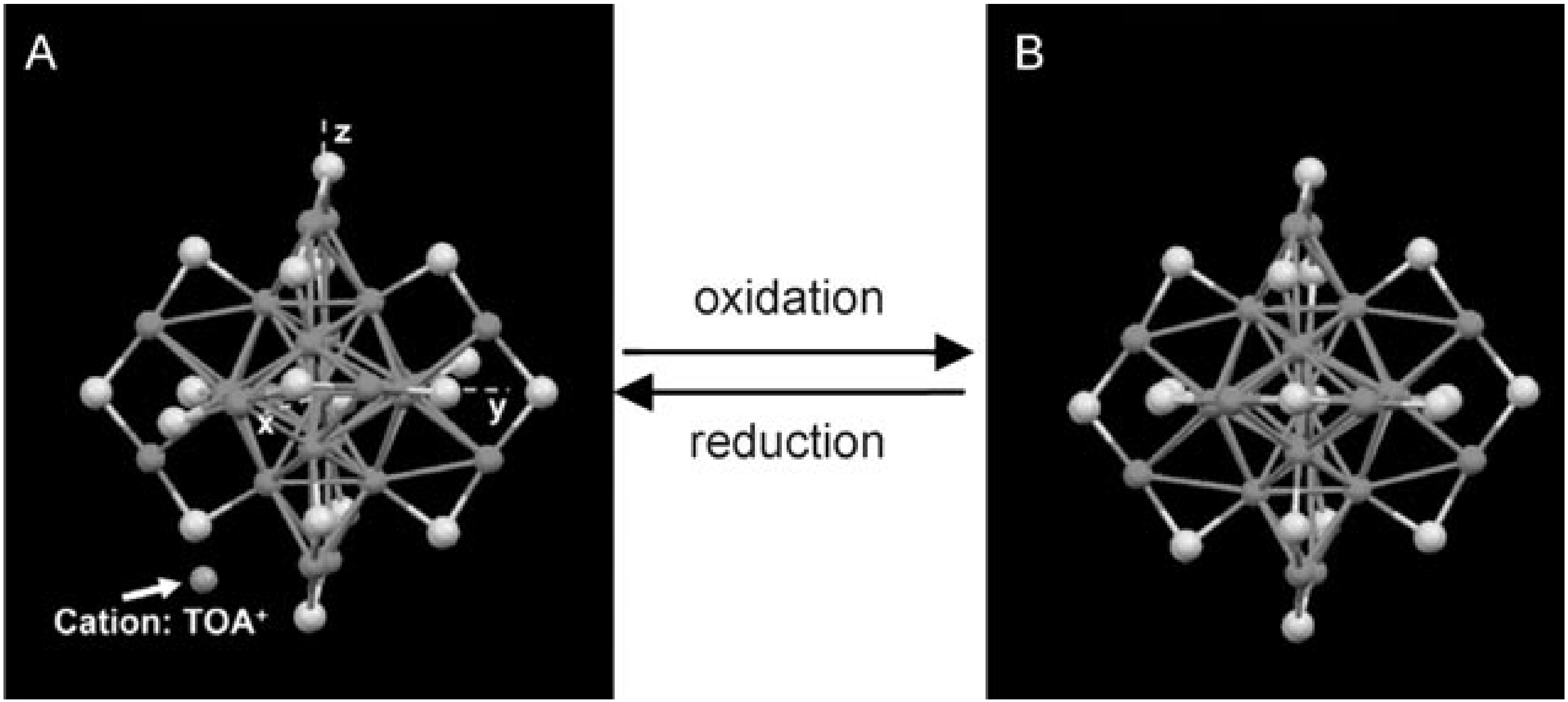
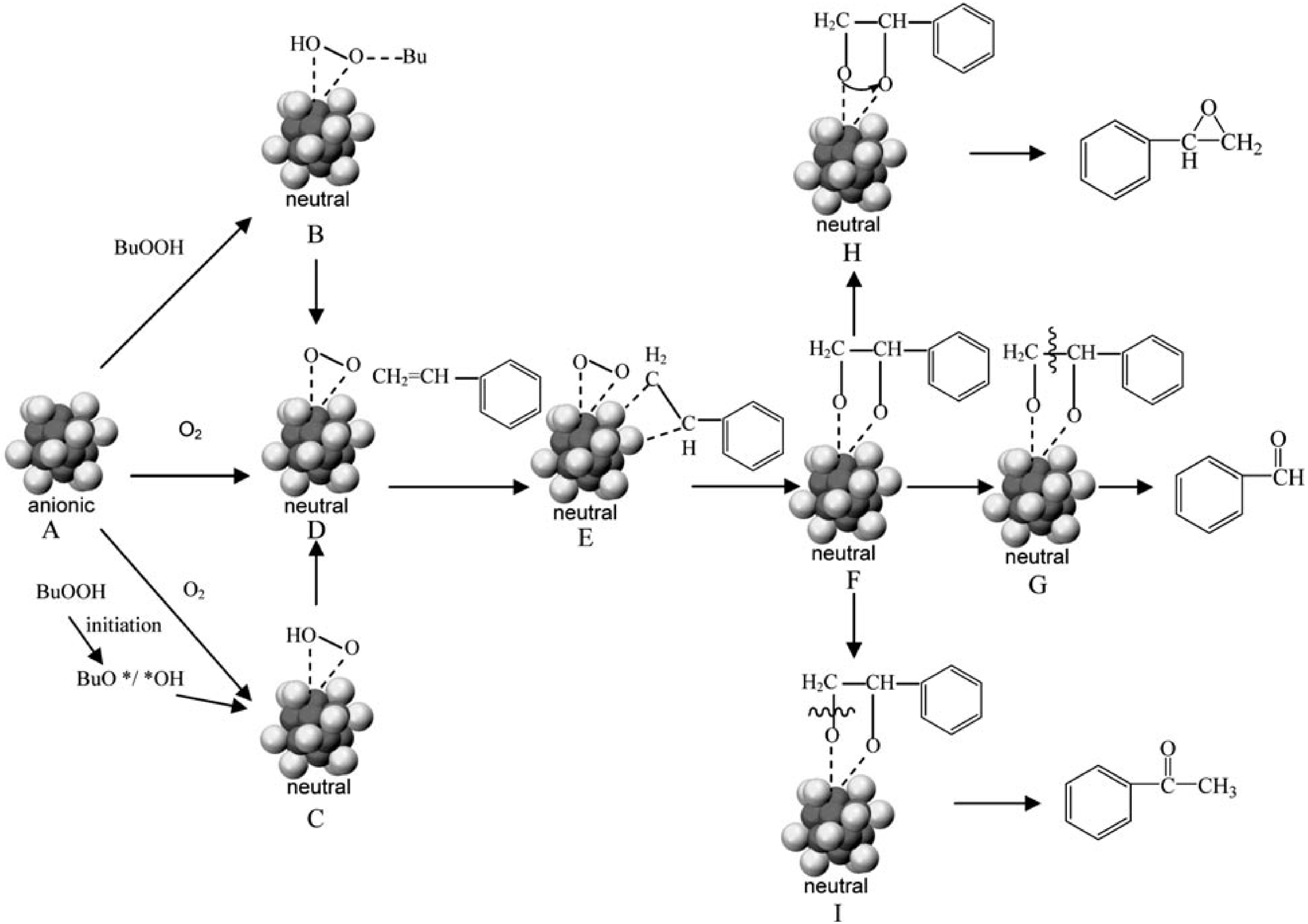


Figure 7. Reversible conversion between the anionic and neutral $Au_{25}(SR)_{18}$ clusters and the crystal structures of anionic (A) and neutral (B) $Au_{25}(SR)_{18}$ clusters (TOA^+ = tetraoctylammonium).



Scheme 1. Proposed mechanism of selective oxidation of styrene catalyzed by a $Au_{25}(SR)_{18}$ cluster. For clarity, the thiolate ligands are not shown. (Dark gray: Au atoms of the core, light gray: Au atoms of the shell)

Thanks