Supporting Information

for

CO Oxidation Catalyzed by Silver Nanoclusters: Mechanism and Effects of Charge

Dianyong Tang, \textsuperscript{a} Zhongzhu Chen,\textsuperscript{b} Jianping Hu,\textsuperscript{a} Guofeng Sun,\textsuperscript{a} Shenzhuang Lu\textsuperscript{a} and Changwei Hu\textsuperscript{c}

\textsuperscript{a}Centre for Functional Molecular Design, Department of Chemistry, Leshan Normal College, Leshan 614000, P. R. China

\textsuperscript{b}Department of New Drug Development, Haimen Wisdom Pharmaceutical Co., Ltd., Haimen 226100, P. R. China

\textsuperscript{c}Key Laboratory of Green Chemistry and Technology (Sichuan University), MOE, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China

*Corresponding Author: Tel & Fax: +86-833-2272106, qchem@189.cn or tangdy2008@163.com (D. Tang); Tel: +86-18981384068, hujianping@email.bjut.edu.cn or lion_hjp@yahoo.com.cn (J. Hu).
S1. Validation of Theoretical Method

To support our choice for the combination of the functional and basis sets described in the computational details, we provide benchmark calculations of the electron affinities (EAs) and ionization potentials (IPs) for Ag, Ag₂, Ag₃, and O₂, and of the geometrical parameters for O₂, CO, and CO₂. As shown in Table S1, the calculated IPs and EAs are in good agreement with the previous experimental values. The Ag-Ag bond length and bond energies of Ag₂ are predicted to be 2.578 Å and 1.66 eV, which are in fair agreement with experimental findings (2.480 Å and 1.69 eV)¹. The predicted ground state of Ag₃ cluster is "B₂ state with C₂ᵥ point group, which is in line with the CCSD(T) results.² The Ag-Ag bond length of the Ag₃ ground state is 2.648 Å, which is close to that (2.643 Å) obtained at CCSD(T)/aVQZ level.² The experimental and computational values of the atomization energy [3*E(Ag)-E(Ag₃)] for Ag₃ cluster are 2.62±0.13 and 2.34 eV, respectively.³ The calculated (experimental) bond lengths of C-O in CO, O-O in O₂, and C-O in CO₂ are 1.138(1.128), 1.226(1.207), and 1.176(1.169) Å,⁴ respectively. The calculated (experimental) bond lengths of Ag-O in AgO are 1.995(2.005) Å.⁵ In summary, these facts indicate the acceptable accuracy and reliability of the level of theory used.
Table S1 Calculated and Experimental Electron Affinities (EAs, eV) and Ionization Potentials (IPs, eV) for Ag, Ag₂, Ag₃, AgO, and O₂

<table>
<thead>
<tr>
<th>Species</th>
<th>calculated</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>IP (eV)</td>
</tr>
<tr>
<td>Ag</td>
<td>0.17</td>
<td>7.75</td>
</tr>
<tr>
<td>Ag₂</td>
<td>0.38</td>
<td>7.67</td>
</tr>
<tr>
<td>Ag₃</td>
<td>1.71</td>
<td>5.76</td>
</tr>
<tr>
<td>O₂</td>
<td>0.84</td>
<td>12.76</td>
</tr>
<tr>
<td>AgO</td>
<td>1.06</td>
<td>9.10</td>
</tr>
</tbody>
</table>

ᵃ ref. 6 ᵇ ref. 7 ᶜ ref. 8 ᵈ ref. 9 ᵉ ref. 10 ᶠ CCSD(t)/ aVQZ level in ref.2 ᵍ ref.4 ʰ ref.11 ¹ ref.12

References

3. K. Hilpert and K. A. Gingerich, Berichte Bunsengesellschaft für Physikalische Chemie, 1980, 84, 739.


**S2. Figs. S1 and S2**

![Diagram showing optimized structures](image)

**Fig. S1.** Optimized structures and the related parameters of the Ag$^{55^-}$-catalyzed CO oxidation.
Fig. S2. Optimized structures and the related parameters of the Ag$_{55}^{+}$-catalyzed CO oxidation.