H₂ Dissociation by Au₁-Doped Closed-Shell Titanium Oxide Cluster Anions

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Dissociation of molecular hydrogen (H₂) is extensively studied to understand the mechanism of hydrogenation reactions. In this study, H₂ dissociation by Au₁-doped closed-shell titanium oxide cluster anions AuTi₃O₇⁻ and AuTi₃O₈⁻ has been identified by mass spectrometry and quantum chemistry calculations. The clusters were generated by laser ablation and mass-selected to react with H₂ in an ion trap reactor. In the reaction of AuTi₃O₈⁻ with H₂, the ion pair Au⁺⁻O₂²⁻ rather than Au⁺⁻O²⁻ is the active site to promote H₂ dissociation. This finding is in contrast with the previous result that the lattice oxygen is usually the reactive oxygen species in H₂ dissociation. The higher reactivity of the peroxide species is further supported by frontier molecular orbital analysis. This study provides new insights into gold catalysis involving H₂ activation and dissociation.

Key words: Gold, H₂ dissociation, Closed-shell anions, Mass spectrometry, Density functional theory calculations

I. INTRODUCTION

Oxide supported gold catalysts have been extensively studied owing to their excellent performance in many reactions including hydrogenation [1–4] and formation of hydrogen peroxide [5]. Dissociation of molecular hydrogen (H₂) is usually the rate determining step in catalytic hydrogenation [6, 7] and great efforts have been devoted to investigating the nature of gold catalysis in H₂ dissociation [8–12]. The perimeter sites [8–13] in between gold particles and oxide supports are generally important for catalytic reactions while the molecular-level mechanism of H₂ dissociation by the gold-oxide perimeter sites is unclear owing to the complexity of real-life catalysts.

Gas-phase clusters that can be studied under isolated and well controlled conditions are ideal models to uncover the mechanistic details in the related condensed-phase systems [14–20]. Gold-doped heteronuclear metal oxide clusters are being actively studied to understand the molecular-level mechanism of bond activation by the gold-oxide perimeter sites [21–32]. In the reactions of AuCeO₂⁺ [21], AuNbO₄⁺ [22], Au₂VO₄⁺ [23], AuV₂O₅⁺ [24], and AuVO₄⁺ [25] with H₂, the separated ion pair Au⁺⁻O₂⁻ can dissociate H₂ in a heterolytic manner. Some of the studied oxygen-rich clusters including AuNbO₄⁺ [22], Au₂VO₄⁺ [23], and AuVO₄⁺ [25] contain superoxide (O₂⁻) units. It turns out that the Au⁺⁻O₂⁻ ion pair is usually much less reactive than the Au⁺⁻O²⁻ ion pair for H₂ dissociation. It is noteworthy that the reported metal oxide clusters [33–39] that can dissociate H₂ have open-shell electronic structures except for the positively charged cluster AuCeO₂⁺ [21]. Negatively charged cluster anions are usually much less reactive than the cationic counterparts toward reductive molecules [40] and it is rare to identify closed-shell cluster anions that are reactive with stable molecules such as H₂. Herein, we report that the closed-shell AuTi₃O₇⁻ and AuTi₃O₈⁻ anions can dissociate H₂ under thermal collision conditions. Direct H–H bond cleavage by the Au⁺⁻O₂²⁻ ion pair has been identified for the reaction of AuTi₃O₈⁻ with H₂. This study provides new insights into gold catalysis involving H₂ activation and dissociation.

II. METHODS

A. Experimental methods

The Au₄⁸⁺Ti₃O₈⁻ clusters were generated by laser ablation of a mixed-metal disk compressed with Au and ⁴⁸Ti powders (Au:⁴⁸Ti=1:1 in molar ratio) in the presence of 0.2% O₂ seeded in a He carrier gas with a backing pressure of 6.0 standard atmospheres. The
clusters of interest (AuTi$_3$O$_7^-$ and AuTi$_3$O$_8^-$) were mass-selected with a quadrupole mass filter (QMF) and then entered into a linear ion trap (LIT) reactor, where they were confined and cooled by collisions with a pulse of He atoms for around 1.0 ms and then interacted with a pulse of H$_2$ or D$_2$ for a period of time (1.6–4.7 ms). The temperature of cooling gas (He), reactant gases (H$_2$, D$_2$, or N$_2$), and the LIT reactor was around 298 K. The clusters ejected from the LIT were detected by a reflectron time-of-flight mass spectrometer (TOF-MS). The details of running the TOF-MS [41], QMF [39], and LIT [42] can be found in our previous work. The pseudo-first-order rate constants were determined by a least-square fitting procedure [43].

B. Computational methods

Density functional theory (DFT) calculations using the Gaussian 09 [45] program were carried out to study the mechanisms of the reactions between AuTi$_3$O$_7$, AuTi$_3$O$_8$, and H$_2$. The TPSS functional was found to be appropriate to reproduce the dissociation energies of various chemical bonds including Au–H, Au–O, O–H, Ti–O, and O–O [21, 27]. Thus, the TPSS functional was adopted in this work. The TZVP basis set [46] for Ti, H, and O atoms and the D95V basis set [47] combined with the Stuttgart/Dresden relativistic effective core potentials (denoted as SDD in Gaussian software) for Au atom were used in the calculations. The relaxed potential energy surface scan was used extensively to obtain good guess structures of intermediates and transition states along the reaction pathways. The transition states were optimized using the Berny algorithm [48]. Intrinsic reaction coordinate calculations [49, 50] were performed to confirm that each transition state connects two appropriate local minima. Vibrational frequency calculations were carried out to check that the intermediates and transition states have zero and only one imaginary frequency, respectively. Furthermore, the single point energies of the low-lying isomers of AuTi$_3$O$_7$ and AuTi$_3$O$_8$ clusters were recalculated by the high-level coupled-cluster method with single, double, and perturbative triple excitations (CCSD(T)).

III. RESULTS

The TOF mass spectra for the interactions of laser ablation generated and mass-selected AuTi$_3$O$_7^-$ and AuTi$_3$O$_8^-$ clusters with N$_2$, H$_2$, and D$_2$ are shown in FIG. 1. On the interaction of AuTi$_3$O$_8^-$ with 0.03 Pa H$_2$ for about 4.7 ms (FIG. 1(b)), signals of Ti$_3$O$_7$H$^-$ and Ti$_3$O$_8$H$^-$ as well as AuTi$_3$O$_6^-$ and AuTi$_3$O$_7^-$ could be identified. When high pressure H$_2$ was used (0.60 Pa, FIG. 1(c)), the signal intensity of AuTi$_3$O$_6^-$ increased significantly while that of AuTi$_3$O$_7^-$ nearly disappeared, indicating that AuTi$_3$O$_6^-$ was due to the secondary reaction of the resulting AuTi$_3$O$_7^-$ with H$_2$ (reaction (1a) and then reaction (2a)). The generation of Ti$_3$O$_7$H$^-$ and Ti$_3$O$_8$H$^-$ ions in AuTi$_3$O$_8^-$ + H$_2$ suggests formation of neutral species AuOH (reaction (1b)) and AuH (reaction (1c)), respectively.

\[
\begin{align*}
\text{AuTi}_3\text{O}_8^- + \text{H}_2 & \rightarrow \text{AuTi}_3\text{O}_7^- + \text{H}_2\text{O} \quad (1a) \\
\text{AuTi}_3\text{O}_8^- + \text{H}_2 & \rightarrow \text{Ti}_3\text{O}_7\text{H}^- + \text{AuOH} \quad (1b) \\
\text{AuTi}_3\text{O}_8^- + \text{H}_2 & \rightarrow \text{Ti}_3\text{O}_8\text{H}^- + \text{AuH} \quad (1c) \\
\text{AuTi}_3\text{O}_7^- + \text{H}_2 & \rightarrow \text{AuTi}_3\text{O}_6^- + \text{H}_2\text{O} \quad (2a)
\end{align*}
\]

Products Ti$_3$O$_7$H$^-$, Ti$_3$O$_8$H$^-$, AuTi$_3$O$_6^-$, and AuTi$_3$O$_7^-$ did not appear in the reaction of AuTi$_3$O$_8^-$ with N$_2$ (FIG. 1(a)), indicating that these signals are due to the chemical reaction rather than collision-induced dissociation. The assignment of the product ions was confirmed by the isotopic-labeling experiment (FIG. 1(d)). On the interaction of mass-selected AuTi$_3$O$_7^-$ with 0.01 Pa H$_2$ (FIG. 1(f)), the product of AuTi$_3$O$_6^-$ was identified. This provides further support that the AuTi$_3$O$_6^-$ in FIG. 1(b) was due to the secondary reaction of the resulting AuTi$_3$O$_7^-$ with H$_2$. With respect to AuTi$_3$O$_8^-$ + H$_2$ (FIG. 1(c)), much lower H$_2$ pressure (0.01 Pa) and shorter reaction time (~1.7 ms) were used in AuTi$_3$O$_7^-$ + H$_2$ to have significant signal depletion of the reactant cluster (AuTi$_3$O$_7^-$). This means that AuTi$_3$O$_8^-$ + H$_2$ is much faster than AuTi$_3$O$_6^-$ + H$_2$, which well rationalizes the disappearance of AuTi$_3$O$_7^-$ in FIG. 1(c). In addition to AuTi$_3$O$_6^-$, Ti$_3$O$_7$H$^-$ was also observed in the reaction.
and kinetic isotope effect (KIE) for the reactions of AuTi$_3$O$_3$ and AuTi$_3$O$_7$ cluster anions with H$_2$ or D$_2$.

$$\text{AuTi}_3\text{O}_3^+ + \text{H}_2 \rightarrow \text{Ti}_3\text{O}_3\text{H}^- + \text{AuH} \quad (2b)$$

The pseudo-first-order rate constants ($k_1$) for the reactions of AuTi$_3$O$_7$ with H$_2$ and D$_2$ can be well fitted (FIG. S1 and FIG. S2 in supplementary materials) and the results are presented in Table I. It turns out that about 57% of experimentally generated AuTi$_3$O$_3^-$ could react with H$_2$ and the reactive component for AuTi$_3$O$_7^-$ is about 78%. It has been often reported that a cluster can have different isomeric structures with very different reactivity [26, 51]. For the reactive component of AuTi$_3$O$_3^-$, the $k_1$ value is $(0.061 \pm 0.018) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with the reaction efficiency [52] of 0.41%. The kinetic isotope effect $k_1$(AuTi$_3$O$_3^-$+H$_2$)/$k_1$(AuTi$_3$O$_3^-$+D$_2$) is 1.2. The $k_1$ value for AuTi$_3$O$_7^-$+H$_2$ is $(5.8 \pm 1.7) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with the reaction efficiency of 39%. The kinetic isotope effect $k_1$(AuTi$_3$O$_7^-$+H$_2$)/$k_1$(AuTi$_3$O$_7^-$+D$_2$) is 1.2.

The DFT calculated reaction pathways for H$_2$ dissociation by AuTi$_3$O$_3^-$ and AuTi$_3$O$_7^-$ are shown in FIG. 2 and FIG. 3, respectively. The cluster isomers of AuTi$_3$O$_3^-$ and AuTi$_3$O$_7^-$ have been carefully calculated in our previous study [27] and both of the clusters have closed-shell electronic structures. In the lowest-lying isomer of AuTi$_3$O$_3^-$ (IS1, FIG. 2(a)), the gold atom is bridgingly bounded with one lattice oxygen (O$^2-$) and one peroxide unit (O$_2^2-$ with O–O bond length of 148 pm). Such gold atom can hardly trap H$_2$ (the binding energy is smaller than 0.04 eV). In contrast, the isomers with the terminally bonded gold atom (IS2 and IS3) can trap and react with H$_2$. The positively charged gold (natural charge: +0.39 e) in AuTi$_3$O$_3^-$ (IS2) can anchor H$_2$ tightly with a binding energy of 0.92 eV (I1, FIG. 2(b)). The H–H bond in I1 is significantly activated because the H–H bond length increases from 7 pm in free H$_2$ to 89 pm in I1. In the next step, the gold atom delivers the attached H$_2$ to the O$_2^2-$ unit and then H–H bond cleaves with a barrier of 0.13 eV (I1→TS1→I2, FIG. 2(b)). The formed OOH species is an important intermediate in the condensed phase [11] and the O–O bond cleavage occurs with a barrier of 0.55 eV (I2→TS2→I3). The subsequent steps (from I3 to I7) mainly involve the H atom transfer with a nearly downhill pathway to form a very stable intermediate I7 (−3.46 eV) with two O–H units. The I7 can transform into I8 that can evaporate the AuOH unit favorably to produce the experimentally observed major product ion Ti$_3$O$_7$H$^-$.

Starting from intermediate I2, the reaction complex can also form I9 (I2→TS8→I9) that can evap-

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TABLE I Branching ratios (BRs), total rate constants ($k_1$, in unit of $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), reaction efficiency ($\Phi$), and kinetic isotope effect (KIE) for the reactions of AuTi$_3$O$_3^-$ and AuTi$_3$O$_7^-$ cluster anions with H$_2$ or D$_2$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>X</th>
<th>BRs/%</th>
<th>$k_1$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$\Phi/%$</th>
<th>KIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuTi$_3$O$_8^-$+X$_2$</td>
<td>H</td>
<td>77</td>
<td>4</td>
<td>0.061±0.018</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>77</td>
<td>19</td>
<td>0.054±0.015</td>
<td>0.34</td>
</tr>
<tr>
<td>AuTi$_3$O$_7^-$+X$_2$</td>
<td>H</td>
<td>78</td>
<td>22</td>
<td>5.8±1.7</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>81</td>
<td>19</td>
<td>4.7±1.4</td>
<td></td>
</tr>
</tbody>
</table>

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The relative energy of the critical transition state (TS3: $-0.94$ eV) in the pathway to generate Ti$_3$O$_2$H$^-$ is significantly lower than the energy of TS8 ($-0.65$ eV) and AuTi$_3$O$_7^-$ can further react with H$_2$ to form Ti$_3$O$_2$H$^-$, so the Ti$_3$O$_2$H$^-$ signal can be much stronger than the AuTi$_3$O$_7^-$ signal in FIG. 1(b). Starting from intermediate I1, the reaction complex can also form I10 (I1$\rightarrow$TS9$\rightarrow$I10, FIG. 2(c)) that can cleave the H–H bond through the Au$^+$–O$^{2-}$ ion pair (I10$\rightarrow$TS8$\rightarrow$I11). The intermediate I11 can evaporate AuH to form the experimentally observed product ion Ti$_3$O$_2$H$^-$. From Rice-Ramsperger-Kassel-Marcus theory, the conversion rate of I10$\rightarrow$TS10$\rightarrow$I11 should be faster than that of I2$\rightarrow$TS8$\rightarrow$I9, which is consistent with the result that the Ti$_3$O$_2$H$^-$ signal is stronger than the AuTi$_3$O$_7^-$ signal in FIG. 1(b).

The lowest-lying isomer of AuTi$_3$O$_2^-$ (IS5, FIG. 3(a)) at the CCSD(T) level corresponds to the reactive isomer of AuTi$_3$O$_2^-$ (FIG. 3(b)). FIG. 3(b) shows that the generation of Ti$_3$O$_2$H$^-$+AuH (P4, $-0.95$ eV) is slightly less facile than the generation of AuTi$_3$O$_6^-$+H$_2$O (P5, $-0.97$ eV). However, generation of P5 involves tight transition states TS13 and TS14 should be entropically less favorable than generation of P4, which is consistent with the experimental result (FIG. 1(f)). It should be pointed out that the experiments (FIG. 1) indicated that the reactive component of AuTi$_3$O$_2^-$ is much more reactive than that of AuTi$_3$O$_6^-$ in the reaction with H$_2$. However, the current DFT results (FIG. 2 and FIG. 3) cannot well explain this difference. It is possible that the IS1 or IS4 (FIG. 2) is the reactive component of AuTi$_3$O$_2^-$ and the H$_2$ adsorption and Au–O bond breaking that can also lead to formation of the intermediate I1 may be the bottleneck of AuTi$_3$O$_2^-$+H$_2$ (FIG. S6 in supplementary materials).

**IV. DISCUSSION**

In the field of gas-phase studies, different oxygen species have been proposed to activate and dissociate H$_2$. In the reactions of OsO$_4^+$ [38] and V$_4$O$_{10}^+$ [39] with H$_2$, the atomic oxygen radical O$^-$ is the reactive oxygen species (ROS). Recent studies on the reactions of gold-doped heteronuclear metal oxide clusters highlighted the importance of lattice oxygen O$^{2-}$ in direct H–H bond dissociation [21–25], paralleling the behavior of H$_2$ dissociation in the condensed phase systems [54, 55]. Furthermore, indirect participation of the superoxide radical (O$_2^-$) has also been proposed [22, 23, 25]. Herein, in the reaction of AuTi$_3$O$_6^-$ with H$_2$, direct H–H bond cleavage by the Au$^+$–O$_2^-$ ion pair with peroxide unit has been identified and this pathway is more facile than that by the Au$^+$–O$^{2-}$ ion pair.

To further understand the mechanism of H$_2$ dissociation by AuTi$_3$O$_6^-$, the natural charges on the Au atom, the two hydrogen atoms, and the O$_2^{2-}$ unit during H$_2$ dissociation (I1$\rightarrow$TS1$\rightarrow$I2) are monitored and provided in FIG. 4(a). In the intermediate I2, the positively charged H atom in the OOH unit (H2, $+0.50$ e) and the negatively charged H atom (H1, $-0.26$ e) in the AuH unit are good indicators of heterolytic cleavage of the H–H bond, which is the most common mechanism of H$_2$ dissociation by gold-containing species in both of the gas-phase and the condensed-phase systems [2, 11, 21, 54, 55]. Note that the charge on the O$_2^{2-}$ unit is nearly constant during H$_2$ dissociation ($-0.66$ e in I1 vs. $-0.72$ e in I2), which is consistent with the same O–O bond length (1.49 pm) in I1 and I2, pointing to the fact that a proton (H$^+$) is attached on the O$_2^{2-}$ unit in I2.

The frontier molecular orbital analysis (FIG. 4(b)) shows that for AuTi$_3$O$_8^-$, the lowest unoccupied molecular orbital (LUMO) is on the AuO moiety which can be the electron-acceptor. In contrast, the highest occupied molecular orbital (HOMO) is on the O$_2^{2-}$ unit which can be the electron-donor. Upon H$_2$ adsorption, the LUMO of AuTi$_3$O$_8^-$ accepts the $\sigma$ electrons of H$_2$ and the H$_2$ $\sigma^*$ orbital becomes the LUMO of the intermediate I1. The HOMO of I1 is almost identical to the HOMO of AuTi$_3$O$_8^-$.

FIG. 3 DFT calculated potential energy profiles of (a) transformation between two low-lying isomers of AuTi$_3$O$_7^-$ and (b) the reaction AuTi$_3$O$_7^-$+H$_2$ on the singlet spin state. The relative energies for cluster isomers IS5, IS6, intermediates (I12–I15), transition states (TS11–TS13), and products are in unit of eV. Bond lengths are given in unit of pm. P4: Ti$_3$O$_2$H$^-$+AuH; P5: AuTi$_3$O$_6^-$+H$_2$O. The values in the square brackets (a) are the single-point energies calculated at the CCSD(T) level.
reaction of AuTs3+ acid-base ion pair of Au heterolytic manner through cooperation of the Lewis stable di-hydrogen. The H2 electronic structures can activate and dissociate the very strong bond. To the best of our knowledge, this is the first report that the cluster anions with closed-shell electronic structures can activate and dissociate the very stable di-hydrogen. The H–H bond is cleaved in a heterolytic manner through cooperation of the Lewis acid-base ion pair of Au+–O2− or Au+–O22−. In the reaction of AuTs3O8− with H2, the ion pair involved with the peroxy unit (Au+–O22−) is more reactive than that with the lattice oxygen (Au+–O2−) for H2 dissociation. This is in contrast with the common consideration that the lattice oxygen is the reactive oxygen species to dissociate H2 in the reaction systems of metal oxides. New insights are provided into gold catalysis involving H2 activation and dissociation.

Supplementary materials: Detailed description of experimental and theoretical methods and additional theoretical results are given.

VI. ACKNOWLEDGMENTS

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