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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2014

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Oxygen−Sulfur Exchange and the Gas-Phase Reactivity of Cobalt Sulfide Cluster Anions with Molecular Oxygen

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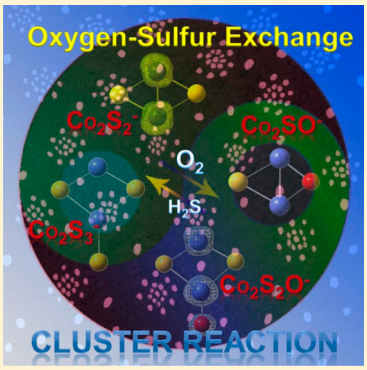
ABSTRACT: We present here a study of gas-phase reactivity of cobalt sulfide cluster anions $Co_mS_n^-$ with molecular oxygen. Nascent $Co_mS_n^-$ clusters were prepared via a laser ablation source and reacted with oxygen in a fast flow reactor under thermal collision conditions. We chose $^{18}O_2$ in place of $^{16}O_2$ to avoid mass degeneration with sulfur, and a time-of-flight (TOF) mass spectrometer was used to detect the cluster distributions in the absence and presence of the reactant. It was found that oxygen−sulfur exchange occurs in the reactions for those with specific compositions $(CoS)_n^-$ and $(CoS)_nS^-$ (n = 2−5) according to a consistent pathway, "$Co_mS_n^- + {}^{18}O_2 \rightarrow Co_mS_{n-1}{}^{18}O^- + S^{18}O$". Typically, for "$Co_2S_2^- + {}^{18}O_2$" we have calculated the reaction coordinates by employing the density functional theory (DFT), where both the oxygen−sulfur exchange and SO molecule release are thermodynamically and kinetically favorable. It is noteworthy that the reaction with molecular oxygen (triplet ground state) needs to overcome a spin excitation as well as a large O−O activation energy. This study sheds light on the activation of molecular oxygen by cobalt sulfides on one hand and also provides insight into the regeneration mechanism of cobalt oxides from the counterpart sulfides in the presence of oxygen gas on the other hand.



1. INTRODUCTION

Transition-metal sulfides are of significance in catalytic processes and biochemical systems.[1−4] In general combination with molybdenum, cobalt sulfides are widely used as catalysts for industrial process such as hydrodesulfurization implemented in large-scale refining.[5−9] The best defined sulfides of cobalt exist in rare minerals, such as the rare mineral cattierite with a main stoichiometry CoS_2.[10] Besides, cobalt sulfides are produced in some industrial and chemical processes, typically in the adsorptive and catalytic removal of H_2S from waste gases in petroleum, gas, and metallurgical industries.[11] In these chemical processes, cobalt sulfides can be generated during the initial stages of H_2S interacting with cobalt oxide surfaces:[12,13]

$$nH_2S + Co_mO_n \rightarrow Co_mS_n + nH_2O \quad (1)$$

In this process of eq 1, the cobalt oxides function as reactants, also adsorbents and catalysts, leading to the production of cobalt sulfides and a conversion of H_2S into H_2O. To elucidate the molecular-level reaction mechanisms involved in the removal of H_2S, recently we have systematically studied the gas-phase reactions of transition-metal oxide cluster anions $M_mO_n^-$ (M = V, Mn, Fe, Co, Ni, Cu, and Zn) and also cationic $M_mO_n^+$ with H_2S.[13−17] It was found that, in addition to H_2S adsorption to form association products, another three types of reactions are evidenced (thermodynamically and kinetically favorable) in the reactor by producing HS, S, and H_2O, respectively. These studies including structures and reactivity of cobalt oxide clusters help provide insights into the mechanisms of H_2S transformation over metal oxide surfaces.

It is equally important to note that cobalt oxides can be regenerated from the cobalt sulfides at low temperatures in the presence of oxygen,[11,18,19]

$$Co_mS_n + 3n/2O_2 \rightarrow Co_mO_n + nSO_2 \quad (2)$$

which indicates application potentials for recycled use via further H_2S adsorption. Such two reaction pathways demonstrate interesting oxygen−sulfur exchange process.[20] However, the detailed molecular-level mechanism for the regeneration of cobalt oxides from cobalt sulfides (i.e., oxygen−sulfur exchange) is still illusive to be further explored.

As is well-known, molecular oxygen is spin triplet in its ground state, and the two half-filled molecular orbitals are antibonding in nature, which means that the activation of molecular oxygen requires to fill the half-filled antibonding orbitals in $^3O_2$ and to reduce the multiplicity of the molecule from triplet to singlet. In this point, previous studies have demonstrated that spin accommodation determines the reactivity of metal cluster anions with oxygen.[21,22] For example, Ag_n^- clusters with even numbers of Ag atoms (odd numbers of electrons) are much more reactive than their counterparts of odd atoms (even numbers of electrons); together with theoretical studies, it has been found that this behavior is correlated with the spin excitations needed to activate the O−O

Special Issue: A. W. Castleman, Jr. Festschrift

Received: January 24, 2014
Revised: February 18, 2014

   dx.doi.org/10.1021/jp500837g | J. Phys. Chem. A XXXX, XXX, XXX−XXX

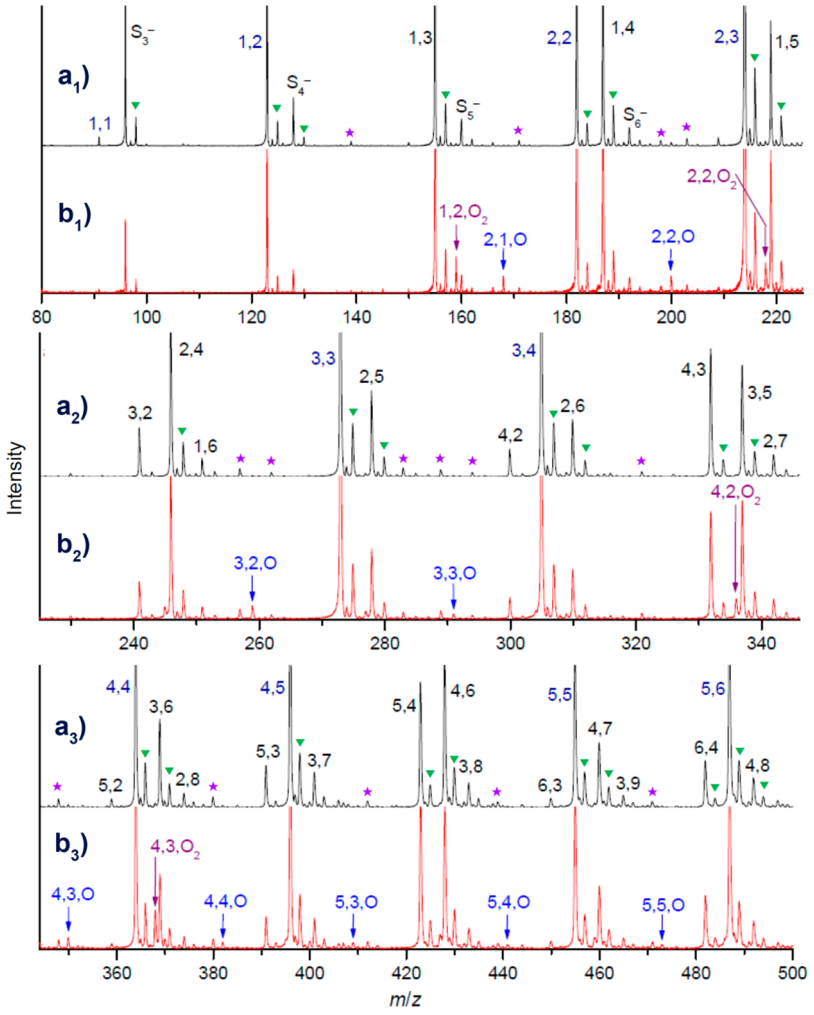


Figure 1. Time-of-flight mass spectra of $Co_mS_n^-$ (m = 1−5) in the absence (a_1, a_2, a_3) and presence (b_1, b_2, b_3) of molecular oxygen $^{18}O_2$. Partial pressure of $^{18}O_2$ in the reactor is approximately 1.2 Pa for b_1−b_3. Symbols m,n, m,n,O, and m,n,O_2 denote $Co_mS_n^-$, $Co_mS_n{}^{18}O^-$, and $Co_mS_n{}^{18}O_2^-$, respectively. In a_1−a_3, the stars and triangles mark the minor peaks of $Co_mS_n{}^{16}O^-$ and $Co_m{}^{34}S_n^-$, respectively.

bond in molecular oxygen.[23] On the other hand, it is well-known that oxidative transformations of stable molecules on surfaces also often involve reactive oxygen species (ROS).[24−29] Specifically, for condensed-phase reactions involving molecular oxygen, the O_2 molecule is considered to dissociate in the following scheme: O_2 (molecular oxygen) → $O_2^{-\bullet}$ (superoxide) → O_2^{2-} (peroxide) → $2O^{-\bullet}$ (mononuclear oxygen-centered radical) → $2O^{2-}$ (lattice oxygen), among which the $O_2^{-\bullet}$, O_2^{2-}, and $O^{-\bullet}$ are ROS.[30] The chemical reactions toward oxygen are ubiquitous with important scientific issues involved.

In this study, we have presented an investigation into the reactions of cobalt sulfide cluster anions $Co_mS_n^-$ with O_2 by a joint experimental and theoretical approach, that is, via time-of-flight (TOF) mass spectrometry and density functional theory (DFT) calculations. As results, the oxygen−sulfur exchange dominates the reactions of $Co_mS_n^-$ (n = 2−5) according to a consistent pathway "$Co_mS_n^- + {}^{18}O_2 \rightarrow Co_mS_{n-1}{}^{18}O^- + S^{18}O$". The regeneration of cobalt oxides (e.g., Co_2O_2) from the counterpart sulfides (e.g., Co_2S_2) simply in the presence of molecular oxygen suggests valuable cluster species for repeated use in H_2S pollution treatment. Also it is expected to validate an effective approach revealing such mechanistic details in condensed-phase reactions by studying their cluster reactivity under well-controlled gas-phase conditions.

2. EXPERIMENTAL AND THEORETICAL METHODS

2.1. Experimental Section. The experiments were conducted by a TOF mass spectrometer (TOF-MS) coupled with a laser ablation cluster source and a fast flow reactor.[31] The $Co_mS_n^-$ clusters were produced by laser ablation of a rotating and translating cobalt sulfide disk (Co/S mole ratio of 2:1) in the presence of a helium carrier gas with a backing pressure of 5 atm. A 532 nm (second harmonic of Nd^{3+}: yttrium aluminum garnet-YAG) laser was used, with an energy of 5−8 mJ/pulse and repetition rate of 10 Hz. The gas was controlled by a pulsed valve (General Valve, Series 9). To prevent residual water in the gas handling system from forming undesirable hydroxo species, the carrier gas He was passed through a 10 m long copper tube coil at low temperature (T = 77 K) before entering into the pulsed valve. Similar treatment was also applied in the use of the reaction gas (1% $^{18}O_2$ seeded in He) that was pulsed into the reactor 20 mm downstream from the exit of the narrow cluster formation channel by a second pulsed valve (General Valve, Series 9). The choice of $^{18}O_2$ as the reaction gas is based on a consideration to avoid the confusion and uncertainty of $Co_mS_n^-$ clusters, as the mass number of $^{16}O_2$ is identical to that of a sulfur atom. With our method as presented previously,[32] the instantaneous total gas pressure in the fast flow reactor was estimated to be around 220

dx.doi.org/10.1021/jp500837g | J. Phys. Chem. A XXXX, XXX, XXX−XXX

Pa at T = 300 K. The intracluster vibrations were likely equilibrated (cooled or heated, depending on the vibration temperature after exiting cluster formation channel with a supersonic expansion) to the bath gas temperature before reacting with the diluted $^{18}O_2$. It is anticipated that the bath gas has the same temperature as the wall of the reactor,[33] and actually our recent experiments indicated that the cluster vibrational temperature in the reactor was close to 300 K.[34,35] After sufficient reaction in the fast flow tube reactor, the reactant and product ions were skimmed into the TOF-MS vacuum system for mass and abundance measurements. The uncertainty of the relative ion signals is no more than ~15% and mass resolution ($M/\Delta M$) is at 400−500 with current experimental setup. More details of the experiments can be found in our previous work.[36]

2.2. Computational Details. DFT calculations with Gaussian 09 program[37] were performed to investigate the reaction mechanisms of "$Co_2S_2^-$ + O_2". The hybrid B3LYP functional[38,39] with the 6-311+G(d) basis set[40] was used in this study. The choice of B3LYP method with moderate computational cost has been tested to provide reasonable results for cobalt sulfides.[41,42] Geometry optimizations of all the reaction intermediates and transition states on the potential energy surfaces were carried out with full relaxation of all atoms. Vibrational frequency calculations were carried out to ensure that the reaction intermediates and transition state species have zero and one imaginary frequency, respectively. The DFT-calculated energies reported in this study are corrected (ΔH_{0K}) on the basis of zero-point vibrational energies (ZPE) and the relative Gibbs free energies (ΔG_{298K}) under a temperature of 298.15 K and pressure of 1.0 atm. Structures and vibrational frequencies for all of the optimized structures are available on request.

3. RESULTS AND DISCUSSION

Figure 1 plots a typical TOF mass spectrum result before (parts a_1−a_3) and after (parts b_1−b_3) reacting with $^{18}O_2$ at a partial pressure of about 1.2 Pa in the reactor. Among the nascent spectrum (Figure 1a, parts a_1−a_3), besides a few peaks due to elemental sulfur, notable $Co_mS_n^-$ series dominate the observed cluster species, and mostly the atom numbers of n are larger than m. In particular, $(CoS)_m^-$ and $(CoS)_mS^-$ series display the maximal intensities. The existence of $(CoS)_mS^-$, similar to $M^+(MX)_n$, resembles the "F-center" localization in bulk alkali metal halide crystals,[43−49] but there is difference as the interaction of excess electrons plays an important role in the outcome of cobalt sulfide clusters. Considering cobalt has an electronic configuration of $1s^22s^22p^63s^23p^63d^74s^2$ and its metal oxidation state generally displays +2 or +3, it is reasonable to form such stable species as Co_2S_2 and Co_2S_3, etc.

Ion molecule reactions often generate simple addition products,[50,51] and such products are seen in our experiments, e.g., $Co_2S_2{}^{18}O_2^-$, $Co_4S_3{}^{18}O_2^-$, etc. However, besides this simple addition reaction pathway, several product peaks assigned to $Co_mS_{n-1}{}^{18}O^-$ were observed, especially for those clusters with specific compositions $(CoS)_n^-$ and $(CoS)_nS^-$ (n = 2−5), suggesting an interesting oxygen−sulfur exchange reaction channel, expressed as

$$Co_mS_n^- + {}^{18}O_2 \rightarrow Co_mS_{n-1}{}^{18}O^- + S^{18}O \quad (3)$$

To further illustrate this interesting reactivity, Figure 2 displays an enlarged area for 167−183 amu, where the relative

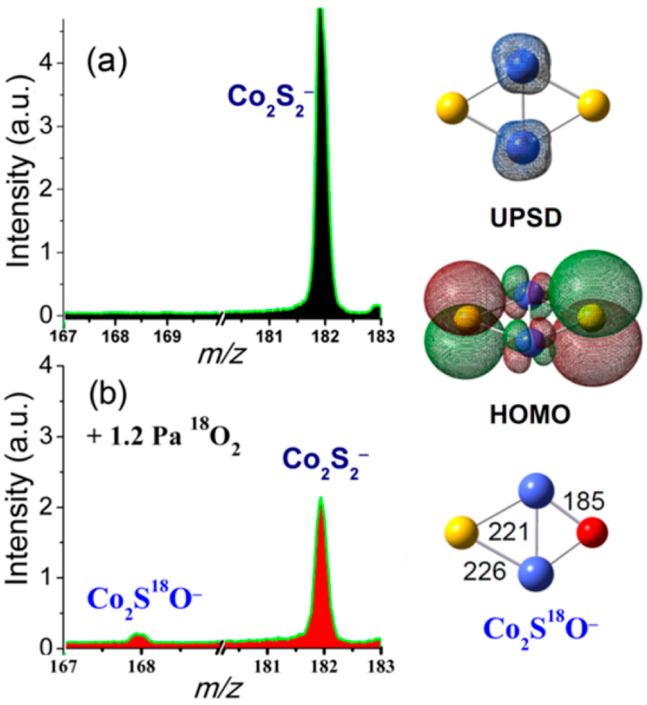


Figure 2. Enlarged area in Figure 1a,b, displaying the relative intensity in the reaction. The insets on the right display the chemical structures of $Co_2S_2^-$ and Co_2SO^-. The unpaired spin density distribution (UPSD) and the highest occupied molecular orbital (HOMO) for $Co_2S_2^-$ are also displayed.

intensity of $Co_2S_2^-$ is apparently reduced when reacting with $^{18}O_2$, together with a production of $Co_2S^{18}O^-$. This finding leads to our in-depth study on the cluster reactivity of "$Co_2S_2^-$ + O_2" as discussed below. It is worth mentioning that the total intensity of the product $Co_2S^{18}O^-$ and remaining $Co_2S_2^-$ (even including $Co_2S_2{}^{18}O_2^-$ as seen in Figure 1) is still not as large as the nascent $Co_2S_2^-$, indicating that unreactive scattering is involved.[52,53]

To elucidate the experimental results that oxygen−sulfur exchange reactions can readily take place under thermal collision conditions, DFT calculations were emphasized on the following reaction:

$$^6Co_2S_2^- + {}^3O_2 \rightarrow {}^6Co_2SO^- + {}^3SO$$
$$\Delta H_{0K} = -0.07 \text{ eV} \quad (4)$$

The superscripts indicate the spin multiplicities for the reactant and product species, and the ΔH_{0K} value refers to the DFT calculated enthalpy. The DFT calculated reaction coordinates for "$Co_2S_2^-$ + O_2" are shown in Figure 3 where the energies are directly marked out. Upon the approach of O_2 to $Co_2S_2^-$, the Co−O_2 bond forms immediately along with an elongation of the O−O bond from 121 to 132 pm, and this process "$Co_2S_2^-$ + O_2 → $Co_2S_2O_2^-$ (I_1)" aims at a heat release of 1.46 eV (ΔH_{0K}), which is high enough to provide the energy needed for the bond cleavage of O−O. The O−O distance gradually increases (132 pm → 142 pm → 147 pm → 182 pm), and the OS moiety is formed in the most stable intermediate I_3 (I_1 → $TS_{1/2}$ → I_2 → $TS_{2/3}$ → I_3). It is noteworthy that the O_2 moieties in I_1 and I_2 can be denoted as $O_2^{-\bullet}$ (superoxide) and O_2^{2-} (peroxide), respectively, on the basis of the analysis of the unpaired spin densities on O atoms. The energy released during the formation of I_3 assists in the formation of Co−O bond in

dx.doi.org/10.1021/jp500837g | J. Phys. Chem. A XXXX, XXX, XXX−XXX

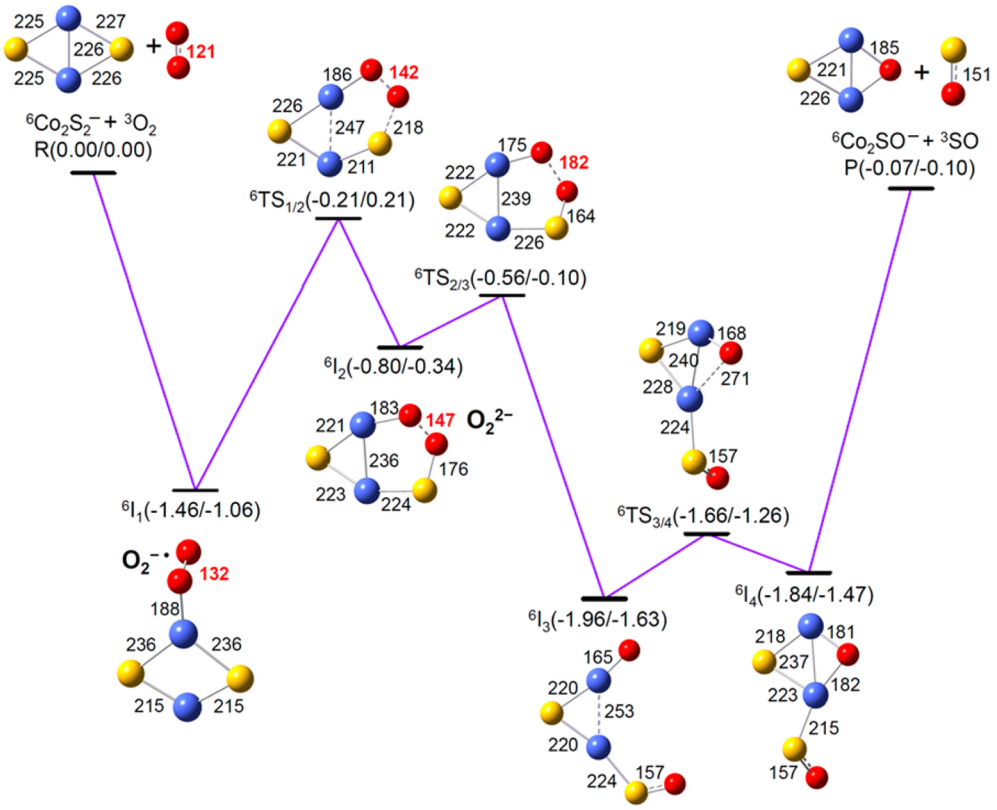


Figure 3. B3LYP/6-311+G(d) calculated oxygen−sulfur exchange reaction pathway for "$^6Co_2S_2^- + {}^3O_2$". The reaction intermediates and transition states are denoted as ^6I_n and $^6TS_{n1/n2}$, respectively. The superscripts 6 and 3 indicate the spin multiplicities for the reaction species from the very beginning to the end of the reaction. The relative energies of ΔH_{0K} and ΔG_{298K} (in electronvolts) with respect to the separated reactants $Co_2S_2^-$ and O_2 are provided in parentheses. Bond lengths are given in picometers.

intermediate I_4 ($I_3 \rightarrow TS_{3/4} \rightarrow I_4$) and the generation of products Co_2SO^- and SO. In addition, the transition states $TS_{1/2}$, $TS_{2/3}$, and $TS_{3/4}$ are lower in energy than the separated reactants $Co_2S_2^-$ and O_2, allowing the oxygen−sulfur exchange reaction to be both kinetically and thermodynamically favorable. The DFT result is consistent with the experimental observation of the generation of Co_2SO^- (Figure $1b_1$ and Figure 2).

It is noteworthy that intermediates I_3 and I_4 are much lower in energy than the products Co_2SO^- + SO and the reactants $Co_2S_2^-$ + O_2. Given that those reaction intermediates carrying not only the binding energy between $Co_2S_2^-$ and O_2 but also the center-of-mass kinetic energy as well as the vibrational energy of the reactants can be stabilized by collisions (rate ~10^7 s^{-1})[35] with the helium bath gas in the reactor, they are possibly observed in the experiment.[17] This is also consistent with the experimental observation of the product peak labeled as "2,2,O_2" in Figure $1b_1$, which is assigned to the aforementioned intermediates I_3 and I_4 (more likely I_3).

Intensity changes of nascent $Co_mS_n^-$ clusters and related products are associated with their reaction rates. With care taken during the repeated experiments, we have examined the intensities of several $Co_mS_n^-$ species before and after reacting with $^{18}O_2$. The pseudo-first-order rate constant (k_1) in the fast flow reactor can be estimated by using the following equation:[32,52]

$$k_1 = -\frac{\ln(I/I_0)}{\rho \times \Delta t} \quad (5)$$

Here, the ratio I/I_0 is the proportion of unreacted clusters after the cluster interaction with reactant gas that has molecular density of ρ in the reactor for reaction time of Δt. The estimated rate constants for $Co_mS_n^-$ with $^{18}O_2$ by using the data in Figure 1 are listed in Table 1. It is shown that $Co_2S_2^-$ is the most reactive cluster toward the oxygen molecule, up to 4.1 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

Table 1. Pseudo-First-Order Rate Constants (k_1/cm^3 $molecule^{-1}$ s^{-1}) for Reactions of $Co_mS_n^-$ with $^{18}O_2$

$Co_mS_n^-$	10^{12} k_1	$Co_mS_n^-$	10^{12} k_1
CoS_2^-	23	$Co_4S_4^-$	10
$Co_2S_2^-$	**41**	$Co_4S_5^-$	6
$Co_2S_3^-$	8	$Co_5S_4^-$	5
$Co_3S_3^-$	7	$Co_5S_5^-$	4
$Co_3S_4^-$	6	$Co_5S_6^-$	3

Besides these typical examples, many other cobalt sulfide clusters also react with molecular oxygen although their reactivities and rate constants differ from each other. Previously, gas-phase investigations have concluded that the reactivity of atomic clusters can be very sensitive to the composition, size, charge, and electronic state details, hence allowing some of them to be more reactive than their counterparts even in the same serial.[53−55] For example, through the studies of Al clusters reacting with D_2O,[56] it was established that size-selective reactivity of clusters could be caused by complementary active sites that refer to two locations on the cluster surface where one location behaves like a Lewis acid (accepting the electrons from

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the oxygen) and an adjacent location behaves as a Lewis base (donating electrons to the hydrogen).[57] Among others, recently in the reaction pathways of VO_4^- with H_2S, the oxygen−sulfur exchange involving peroxide unit in VO_4^- has been unambiguously demonstrated, where all of the four O atoms in VO_4^- can be substituted by S atoms to form VS_4^-.[16] Here in the present work, the peroxide moiety O_2^{2-} derived from the dissociation of O_2 molecule over $Co_2S_2^-$ cluster ($I_1 \rightarrow TS_{1/2} \rightarrow I_2$ in Figure 3) is proposed to be responsible for the oxygen−sulfur exchange reaction; and it may not always be necessary for the molecular oxygen (O_2) to completely dissociate into oxygen-centered radical ($O^{-\bullet}$) or lattice oxygen (O^{2-}) in leading to the oxygen−sulfur exchange reactions.

It is worth mentioning that many investigations have been conducted to understand mechanistic details involved with removal of poisonous H_2S,[20,24] including our recent studies of the cluster reactions between $M_mO_n^-$ (M = Fe, Co, Ni, Cu, and Zn) and hydrogen sulfide.[13] Owing to the contribution of peroxide (O_2^{2-}), oxygen−sulfur exchange found in the reactivity of cobalt sulfides enables regeneration of certain cobalt oxides from their related sulfides and hence displays reutilization potentials. Figure 4 presents such an experimental

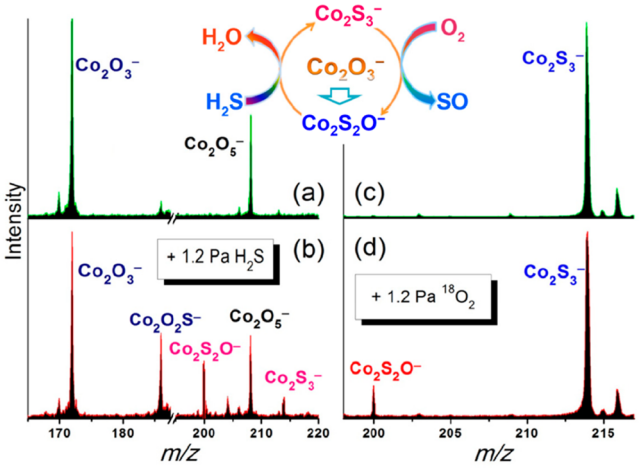

Figure 4. Comparison of the reactions of "$Co_2{}^{18}O_3^-$ + H_2S" (a/b) with "$Co_2S_3^-$ + $^{18}O_2$" (c/d). Intensities of clusters $Co_2O_5^-$ in (a); $Co_2S_2O^-$, $Co_2O_5^-$, and $Co_2S_3^-$ in (b); and $Co_2S_2O^-$ in (d) are scaled by a factor of 3. The data in (a) and (b) are adapted from ref 13.

conception, where $Co_2O_3^-$ reacts with H_2S leading to $Co_2S_2O^-$, which can further react with H_2S to form $Co_2S_3^-$; on the other hand, $Co_2S_3^-$ reacts with oxygen and produces $Co_2S_2O^-$, resulting in recycling reaction pathways.

4. CONCLUSION

Reactivity of cobalt sulfide cluster anions $Co_mS_n^-$ with $^{18}O_2$ under thermal collision conditions was studied by mass spectrometry and density functional theory calculations. The oxygen−sulfur exchange to generate oxygen-containing cobalt sulfide clusters $Co_mS_{n-1}{}^{18}O^-$ was observed in the reactions of clusters with specific compositions $(CoS)_n^-$ and $(CoS)_nS^-$ (n = 2−5). Typically, for "$Co_2S_2^-$ + $^{18}O_2$" we have calculated the reaction coordinates and found consistent results with the experimental observations. Through the joint experimental and theoretical studies, we demonstrate the determining role of peroxide moiety O_2^{2-} for the O−O bond activation in the molecular oxygen reactions "$Co_mS_n^-$ + $^{18}O_2$". This finding of O−O bond cleavage in the gas-phase reactions of cobalt sulfides with $^{18}O_2$ enables the regeneration of certain cobalt oxides from their related sulfides simply by reacting with oxygen.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Chinese Academy of Sciences (Knowledge Innovation Program No. KJCX2-EW-H01), the National Natural Science Foundation of China (No. 21325314), and the 973 Program (Nos. 2011CB932302 and 2013CB834603).

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