Temperature-Dependent Formation of Redox Sites in Molybdenum Trioxide Studied by Electron Paramagnetic Resonance Spectroscopy

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The formation and qualification of redox sites in transition metal oxides are always the active fields related to electronics, catalysis, sensors, and energy-storage units. In the present study, the temperature dependence of thermal reduction of MoO\textsubscript{3} was surveyed at the range of 350\textdegree C to 750\textdegree C. Upon reduction, the formed redox species characterized by EPR spectroscopy are the Mo\textsuperscript{V} ion and superoxide anion radical (O\textsubscript{2}\textsuperscript{-}) when the reduction was induced at the optimal temperature of 300\textdegree C to 350\textdegree C. When heating-up from 350\textdegree C, the EPR signals started to decline in amplitude. The signals in the range of 400\textdegree C to 450\textdegree C decreased to half of that at 350\textdegree C, and then to zero at \~{}600\textdegree C. Further treatment at even higher temperature or prolonged heating time at 500\textdegree C caused more reduction and more free electrons were released to the MoO\textsubscript{3} bulk, which results in a delocalized means similar to the antiferromagnetic coupling. These data herein are helpful to prepare and study the metal-oxide catalysts.

Key words: MoO\textsubscript{3}, Thermal reduction, Mo\textsuperscript{V}, Superoxide anion radical, Electron paramagnetic resonance spectroscopy

I. INTRODUCTION

Molybdenum oxides, one kind of the usual transition metal oxides, are versatile oxide compounds with well recognized applications in many fields, \textit{e.g.} electronics, catalysis, sensors, and energy-storage units [1–6]. Among them, MoO\textsubscript{3} based systems play an important role as active and selective catalysts in redox processes. The active sites therein are usually the variable valence of Mo ions and the O\textsubscript{2}\textsuperscript{-} anion radical in the absence of doping [7, 8], and their formations can be induced by different methods, such as thermal reduction, chemical reduction, or electrolytic reduction [9]. The different reduction processes can determine the following utilizations of the catalysis since the accumulation of the formed redox species is variable. Generally, these active intermediates are amiable to electron paramagnetic resonance (EPR) spectroscopy, and the reduction efficiency and process are therefore to be monitored. Compared to other spectral methods, EPR is a non-invasive technique and is sensitive exclusively to the redox centers and the vicinity. Some of the thermal reductions of MoO\textsubscript{3} had been performed experimentally in a few selective temperatures at the range of 50–350\textdegree C. All these data had implied that the maximal EPR signal was induced thermally at 300–400\textdegree C. The consecutive temperature-dependent behavior however has not been surveyed in detail so far as we know. Moreover, the behavior above 400\textdegree C has not been reported yet, which is important since the applications of the redox materials are practically utilized under the conditions at even higher temperature. Herein, a consecutive temperature dependence from 300\textdegree C to 750\textdegree C was investigated in series of experiments.

II. MATERIALS AND METHODS

A. Preparation and testing

All chemicals used were of AR grade. Ammonium molybdate tetrahydrate ((NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}, AHM) was from J&K, 99.98 atom\% of Mo. Urea was from J&K, 99\% purity. Sodium dodecyl sulfate (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}OSO\textsubscript{3}Na, SDS) was from Sigma-Aldrich, 99.0\% purity.

A mixture of 7.5 g AHM, 2 g urea and 0.1 g SDS was dissolved in 50 mL distilled water, and then the transparent solution was acidified to a pH range of
2.5–3.0 using concentrated HNO₃ solution. The precursor solution was sonicated using a probe sonicator for 30–60 min until MoO₃ was precipitated [10]. The program of sonication runs as follows: pulse mode in 25 s with suspension in 5 s. The glass vessel containing the precipitate was continued for sonication and the temperature of solution was measured at 65–70 °C. After filtration, the precipitate was washed with water and ethanol, and then was dried in oven at 60 °C for 10 h. To induce thermal reduction, the dried precipitate was treated thermally in muffle furnace at different temperatures. After heating, the final products are faint yellow powder. The whole thermal program runs as follows: 25 min from room temperature to 300 °C, maintaining 5 min and constantly increasing to the target temperature in 60 min, then keep it for 4 h. In case the melting point of MoO₃ is 795 °C, the target temperature ranges from 300 °C to 750 °C to avoid the possible sublimation.

The formation of the redox sites which are always paramagnetic in the thermal treated samples was amenable to EPR spectroscopy in a non-invasive way. The room temperature X-band continuous-wave EPR measurements were performed on a Bruker Elexsys EMX spectrometer. The EPR settings are microwave frequency 9.64 GHz, microwave power 2 mW, modulation amplitude 3 G, and average of 4 scans. The samples used for each EPR experiment was 250 mg.

B. EPR theory for anisotropic g-value

The orbital energy levels of Mo⁵⁺ and O₂⁻ are shown in Scheme 1. The principal anisotropic g-values of the O₂⁻ radical were calculated by the following equation:

\[
g_{xx} = g_e \left( \frac{\delta^2}{\lambda^2 + \delta^2} \right)^{1/2} - \frac{\lambda}{\Delta} \left[ -\left( \frac{\lambda^2}{\lambda^2 + \delta^2} \right)^{1/2} \right]
\]

\[
g_{yy} = g_e \left( \frac{\delta^2}{\lambda^2 + \delta^2} \right)^{1/2} - \frac{\lambda}{\Delta} \left[ +\left( \frac{\lambda^2}{\lambda^2 + \delta^2} \right)^{1/2} \right]
\]

\[
g_{zz} = g_e + 2\left( \frac{\lambda^2}{\lambda^2 + \delta^2} \right)^{1/2}
\]

where \(\lambda\) means spin-orbital coupling constant, for O atom, \(\lambda=154 \text{ cm}^{-1}\), and \(l=1\) means p-orbital quantum number. For the orthorhombic Mo⁵⁺, the principal g-values are

\[
g_{xx} = g_e - \frac{2\lambda}{E_{d_{xz}} - E_{d_{yz}}}
\]

\[
g_{yy} = g_e - \frac{2\lambda}{E_{d_{xy}} - E_{d_{xz}}}
\]

\[
g_{zz} = g_e - \frac{8\lambda}{E_{d_{xy}} - E_{d_{yz}}}
\]

where \(\lambda=125 \text{ cm}^{-1}\) for Mo atom, and the denominators are energy difference between the corresponding d-orbitals. For the axial symmetry, \(g_{xx}=g_{yy}\).

![FIG. 1](attachment:image.png)

FIG. 1 The EPR spectra and simulation measured in the multicrystalline MoO₃ samples after 4 h heating at 350 °C. The subscript numbers of 1, 2, and 3 indicate respectively the different components of the EPR absorption (see main text). (a) Experimental spectrum, (b) overall simulation, (c) simulation of the O₂⁻ anion radical, (d) axial Mo⁵⁺ ions, and (e) orthorhombic Mo⁵⁺ ions, respectively. In the spectra, the larger g-values mean the low-field side, and vice versa.

III. RESULTS AND DISCUSSION

In the present study, a rigid temperature-dependent formation of the redox site in molybdenum trioxide was studied by EPR spectroscopy. In principle, the g-values of the EPR spectrum reveal the orbital(s) occupied by the unpaired electron(s), and the hyperfine structure shows the nuclear spin of the nearby atoms magnetically with the unpaired electron. For the single atom possessing the non-zero nuclear spin \(I\), the hyperfine pattern is \((2I+1)\)-splitting [11]. FIG. 1 shows a selec-
A strong and complicated EPR absorption signal is observed in the region around $g=2.0$. After scrutiny, the absorption was assigned to the spectral superposition originated from $O_2^-$ radical and different Mo$^{VI}$ ions, labeled by the subscript number of 1, 2, and 3, respectively. First, at the low-field side of $g=2.0$, $O_2^-$ anion radical gives rise to an anisotropic absorption labeling by the subscript number of 1. With simulation, the characterized rhombic $g$-values are $g_x \approx 2.003$, $g_y \approx 1.979$, and $g_z \approx 2.073$ (the theoretic analysis is given in the above section of EPR theory [12–14]). A triplet hyperfine structure was observed around $g_y \approx 1.979$ with a splitting of $\approx 1.2$ mT, and was assigned to the coordinate $^{14}$N ($I=1$) ligand interacting magnetically with the $O_2^-$ radical [13, 15–19].

In the high-field side of $g_z \approx 2.0$, there are two overlapping signals, one broad and the other narrow in linewidth. When the treated temperature was elevated to 450 °C, the narrow signal disappeared firstly from the spectrum, while the broad one was still present but with a rather diminished amplitude (FIG. 2(a)). The simulation of these two signals was shown respectively in FIG. 1 with the label of the subscript numbers 2 and 3. The obtained parameters (for the narrow, $g_{xx,z}=1.938$, $g_{zz}=1.898$; for the broad, $g_{xx}=1.954$, $g_{zz}=1.932$, $g_{zz}=1.897$) indicated that at least two different 4$d^1$ Mo$^{VI}$ ions are formed, in sites of axial and orthorhombic symmetry in MoO$_3$ bulk respectively. The hyperfine feature arising from the $^{95,97}$Mo isotopes ($I=5/2, 25.2423\%$) is however roughly resolved [13].

With the ensured EPR assignments, the temperature dependence of all the formed paramagnetic species went through, and the results are displayed in FIG. 2(A). The selective experiments at the range of 50–350 °C in the literatures had implied that the maximal EPR signal in amplitude was found after treated thermally at 300–400 °C (which was also confirmed in steps of 50 °C in the present study, and the data are not to be shown). The temperature-dependent behavior above 400 °C has not been reported yet. It is important since the applications of the redox materials are practically utilized under the conditions at even higher temperatures. FIG. 2(A) shows that in the pristine controls over the initial AHM and the dry precipitates, no absorption above the noise level was observed in the EPR spectra (spectrum (a) and (b)). After 4 h heating at 350 °C, the strong and complicated EPR absorption signal is observed in spectrum (c), which has been interpreted thoroughly in the above section. The further results show that the maximal EPR signal was found around ~350 °C. The temperature was thus started to be elevated from 350 °C in 100 °C-steps. After thermal reduction at 450 °C, the amplitudes of all three signals in spectrum (d) decreased to about one-fifth level of those in spectrum (c), and the axil signal labeled by subscript 2 was not observed above the noise level. After raising temperature to 550 °C and above, all these signals disappeared from the spectrum, and a new EPR signal appeared with a sextet hyperfine pattern with a isotropic $g$-value of $\approx 2.004$. When the signal amplitudes of four different fields were plotted as a function of heating temperature, the dramatic decreasing was observed (FIG. 2(B)). After normalization, the decrease to half of the initial signal at 350 °C was reached at the range of 400–450 °C, and then to zero completely at ~600 °C. Additionally, the cubic sextet hyperfine pattern may be the contaminant Mn$^{2+}$ or other isotopes at a trace amount (e.g. $^{17}$O, $^{95,97}$Mo, please note that more than ten of isotopes possess the nuclear spin $I=5/2$, which is hardly identified herein. In principle, the higher temperature treatment can be assumed at an equivalence of the prolonged heating at certain lower temperature. FIG. 3 shows the EPR results as a function of elongation at 500 °C. The dramatic decreasing in signal intensity was observed after 2, 4, and...
FIG. 3 The EPR spectra measured in the samples treated at 500 °C after (a) 2, (b) 4 and (c) 6 h heating respectively.

$$\text{-O}^-\text{[O}^2^-\text{Mo}^{V}\text{]}\text{-O}^- \xrightarrow{\Delta} \text{-O}^-\text{[O}^2^-\text{Mo}^{V}\text{]}^- + \text{O}_2^-$$

Scheme 2 Redox change during the thermal treatment.

6 h heating, respectively. Thermal reduction method is well-established to prepare the reduced intermediates in the metal oxides [3, 15]. To interpret the whole process, the redox change occurring in MoO$_3$ bulk was proposed as Scheme 2 shows. Upon the thermal treatment, the Mo$^{IV}$ ions were reduced firstly to Mo$^{V}$ with the concurrent formation of the O$_2^-$ anion radical, and both are characterized by the EPR measurements. The known oxygen vacancy giving rise to an isotropic EPR signal was not found during the present protocol. The optimize temperature for them was confirmed at a range of 300–350 °C. When the temperature was elevated to 400 °C and higher, the EPR signals started to decrease in amplitude. In principle, the reduction at higher temperatures is to be easier, and the more and more intermediates should be accumulated. This is exactly the case at lower temperature region of 50–350 °C, but not at 350–750 °C. As a result, two possible reasons for the decline are suggested. First, these two species were further reduced to the EPR-silent Mo$^{IV}$ ions and the diamagnetic O$_2^-$ ions. Secondly, the delocalization of the accumulated electrons was induced at high temperature, and resulted in a complicate anti-ferromagnetic coupling structure the MoO$_3$ bulk. This can lead to the metal-like property due to the free delocalized or conduction electrons.

IV. CONCLUSION

The thermal reduction of MoO$_3$ was surveyed at the range of 350 °C to 750 °C. The optimal temperature to induce the Mo$^V$ and O$_2^-$ anion radical was found to be about 300–350 °C. The treatment at higher temperature or the prolonged heating time at certain temperature will cause deeper reduction and more free electrons release to the bulk in a delocalized means similar to the anti-ferromagnetic coupling. The results here are helpful to the researches and the further applications of the metal-oxide catalysts.

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