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Short communication

Hydroxyl radical production in aerobic aqueous solution containing metallic tungsten

Miao Yang *, Inna Soroka, Mats Jonsson

School of Chemical Science and Engineering, Applied Physical Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT

In this work, we investigate the production of hydroxyl radicals from the $W_{(s)}$/air aqueous system by quantifying the amount of scavenging product formaldehyde via the modified Hantzsch method. Tris(hydroxymethyl) aminomethane (Tris) and methanol are used as probe for HO•. Meanwhile, the amount of dissolved tungsten is determined by ICP-OES. A turnover point ([W] ≈ 200 μM) is observed in the Tris case after which the production rate of CH_2O overwhelms the constant rate in the methanol case. Based on the results, a mechanism is proposed for the studied system including both surface and solution reactions.

1. Introduction

Tungsten (W) is of utmost importance in various fields such as photocatalysis [1,2], optics/electronics [3], solar energy [4], nuclear power [5], semiconductors [6] and catalysis [7]. Therefore, the study of the properties of W is of significant scientific and technological interest. Since many applications of W are in heterogeneous systems, there are numerous studies regarding the solution chemistry, pH sensitivity, corrosion, dissolution and so on [8–10].

Some metals, e.g. Fe, Al and Cu, can be quickly oxidized in aerobic aqueous solution to dissolve Fe(II)/Fe(III), Al(III) and Cu(I)/Cu(II), respectively [11–13]. Several reactive oxidants (H_2O_2, HO•, HO_2•) which can oxidize organic and inorganic compounds in solution are produced during this oxidative dissolution process [14]. H_2O_2 is the dominating product which can further react with dissolved redox metal ions pair producing HO• and HO_2• via the Haber–Weiss peroxide chain breakdown [15]. Some factors were reported to affect the oxidative dissolution process, e.g. pH, ligands and particle size [11,14]. However, the reaction of metallic tungsten and oxygen in aqueous solution producing oxidants has to the best of our knowledge not yet been investigated.

The Haber–Weiss peroxide chain breakdown mechanism (R1 and R2) is described as follows [16–18]:

$$M_{ox} + H_2O_2 \rightarrow M_{red} + HO_2\bullet + H^+ \quad (1)$$

$$M_{red} + H_2O_2 \rightarrow M_{ox} + HO\bullet + HO^-. \quad (2)$$

M_{ox} and M_{red} represent the oxidized and reduced forms of the one-electron redox couple in transition metal complexes (e.g., Fe(III)/Fe(II), W(VI)/W(V)). The reactions (R1 and R2) can take place in homogeneous systems as well as in heterogeneous systems at solid–liquid interfaces [19,20]. The rate limiting step is R1 [16] which can be influenced by the formation of ligands with the metal ions or polyoxometalate [15,17,21]. Haber–Weiss peroxide chain breakdown is capable of producing hydroxyl radicals continuously without changing the total iron concentration [22–24].

The oxidants (mainly HO•) yielded from Metal/O_2 system are quantified via monitoring the amount of CH_2O produced by HO• reacting with probes (e.g. methanol, ethanol, benzoic acid and 2-propanol) in pH-buffered solution [11]. Tris is a promising candidate to probe Metal/O_2 system since it is a good pH buffer and hydroxyl radical scavenger [25] In our previous work, the factors (pH and O_2) affecting the yield of converting hydroxyl radicals into formaldehyde in homogeneous system by methanol and Tris have been studied [26]. This yield (Y) can be simply described as $Y = [CH_2O]/[HO\bullet]$. $[CH_2O]$ and $[HO\bullet]$ denote the concentration of generated CH_2O and HO• respectively. The yield (Y) for Tris is both dependent on O_2 concentration and solution pH, based on which, a mechanism of Tris reacting with hydroxyl radical has been proposed [26].

Recently, the $W_{(s)}/H_2O_2$/Tris system has been studied systematically [24]. Due to the significant oxidative dissolution, the concentration of dissolved tungsten is sufficiently high and it was shown that the homogeneous Haber–Weiss peroxide chain breakdown between H_2O_2 and W(VI)/W(V) is dominating the consumption of H_2O_2 as well as the formation of CH_2O except during a short initial period when the oxidative dissolution dominates [24]. Similar to the H_2O_2/Fe(III)/Fe(II) system [22], a slow initial phase of hydroxyl radical production is

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* Corresponding author.
E-mail address: miaoyang@kth.se (M. Yang).

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observed in the H_2O_2/W(VI)/W(V) system [24]. During this period, the W(V) concentration increases until it is sufficient to accelerate the production rate of HO• via R2.

In this work, we investigate the role of metallic tungsten powder in oxidant production from aerobic solution. Tris and methanol are selected as probes to quantify the production of oxidants. The time-resolved concentrations of dissolved tungsten species and formaldehyde are determined by ICP-OES and a UV–vis spectrophotometer, respectively. Based on the results, a mechanism for the aqueous W/O_2 system is proposed.

2. Experimental section

2.1. Instrumentation

The specific surface area of tungsten powder was determined by the Brunauer–Emmett–Teller (B.E.T.) method based on isothermal adsorption and desorption of a gaseous mixture consisting of 30% N_2, 70% He using a Micrometrics Flowsorb II 2300 instrument. The experiments were performed in aqueous solution saturated by N_2 (≥99.999%, Strandmøllen A/S) or air. The powder suspensions were stirred using a Heidolph MR3001K magnetic stirrer at 600 rpm. UV/Vis spectra were collected by using a Thermo Scientific Genesys 20 UV/Vis spectrophotometer. The pH of solution was measured by Metrohm 713 pH Meter with an accuracy of ± 0.1 pH units.

ICP-OES (*Inductively coupled plasma optical emission spectroscopy*, *Thermo Scientific iCAP6000 series*) was used for trace elemental analysis on all solutions. The limitation of ICP-OES is no information regarding the oxidation state of element can be obtained. The analysis for tungsten was performed at wavelengths of 207.9, 209.8 and 224.8 nm using ICP element standard IV from Sigma Aldrich.

2.2. Reagents and experiments

All the solutions used in this study were prepared using Millipore Milli-Q water.

The B.E.T. specific surface area of tungsten powder (CAS[7440-33-7], Aldrich 99.9%, 12 μm) is 0.11 ± 0.01 m^2 g^{-1}. Produced hydroxyl radicals are scavenged by Tris (CAS[77–86–1], BDH Chemicals, 99%) or methanol (CAS[67–56–1], Aldrich, 99%). Acetoacetanilide AAA (CAS[102–01–2], Aldrich, ≥98%) and ammonium acetate (CAS[631–61–8], Aldrich, ≥98%) were used for quantifying formaldehyde with the modified version of the Hantzsch method [27,28]. Ammoniumdimolybdate ADM (Alfa Aesar, 4% *w*/*v*) and potassium iodide (VWR BDH Prolabo, 99.0%) were used in the Ghormley triiodide method [29,30] determining the concentration of H_2O_2.

To study the reactions between metallic W powder and O_2 in aqueous solution in the presence of Tris/methanol, W powder was immersed into aerobic Tris/methanol solution (100 mM, 50 mL). The experiments were performed at ambient temperature in the dark, N_2 atmosphere or air-saturated and continuous magnetic stirring at a rate of 600 rpm. The pH of suspension was adjusted to 7.5 by HCl/NaOH after mixing Tris and W powder (methanol solution without pH adjustment). Samples were taken (5 mL) at predetermined time points which were extracted from the reaction vessel by a syringe and then filtered through a 0.2 μm cellulose acetate syringe filter. Then, sample volume of 1.5 mL was used to measure CH_2O concentration by the modified Hantzsch method (uncertainty < 2%) [27,28] and 3.5 mL was used to measure the amount of dissolved W by ICP-OES. The concentration of H_2O_2 was checked in the end (5–6 h) and it was determined by the Ghormley triiodide method (uncertainty < 2%) [29,30].

3. Results and discussion

The dissolution of tungsten and oxidation of Tris (100 mM) and methanol (100 mM) to CH_2O in the aqueous W/Air or W/N_2 system was investigated and compared. All the results are shown in Figs. 1 and 2, respectively.

It can be seen from Figs. 1 and 2 that, concentrations of dissolved tungsten and produced CH_2O are both significantly enhanced by the presence of O_2 in both the Tris and methanol cases. Given the similarity to previous works [11–14,24], this indicates that hydroxyl radicals are produced continuously which should be attributed to the formation of H_2O_2 and the Haber–Weiss peroxide chain breakdown between H_2O_2 and W(VI)/W(V). The detected H_2O_2 concentration is marginal which should be attributed to the fact that H_2O_2 is rapidly consumed in the present system. As can be seen, there is a slight delay in the production of formaldehyde for both Tris and methanol. This can be attributed to the delay in producing catalytic sites for H_2O_2 decomposition as was recently shown [24].

It has been shown that the rate of the homogeneous Haber–Weiss peroxide chain breakdown between H_2O_2 and W(VI)/W(V) is enhanced in the presence of Tris [24]. The corresponding effect of methanol has not yet been investigated. Therefore, experiments were performed to investigate the impact of methanol. The procedure was the same as in previous work [24]. Extra H_2O_2 was added to the filtered methanol sample after reaction. It should be noted that [CH_2O] in the filtered solution ($[H_2O_2] \approx 0$) was found to be stable after exposure to air overnight. This implies that CH_2O cannot be produced in the reaction between tungsten ions and O_2. The concentrations of H_2O_2 and CH_2O after the addition of H_2O_2 were plotted as function of reaction time (Fig. 3).

As can be seen in Fig. 3, the H_2O_2 concentration becomes relatively stable after an initial drop while the CH_2O concentration is almost constant during the whole process. This indicates that methanol has insignificant impact on the decomposition of H_2O_2 in the present homogeneous system. Therefore, the production of CH_2O in the $W_{(s)}$/air/methanol system should be primarily attributed to the heterogeneous Haber–Weiss peroxide chain breakdown.

In order to obtain more information about the reactions in $W_{(s)}$/air/Tris or $W_{(s)}$/air/methanol system, we plotted the concentration of formed CH_2O against the concentration of dissolved tungsten species

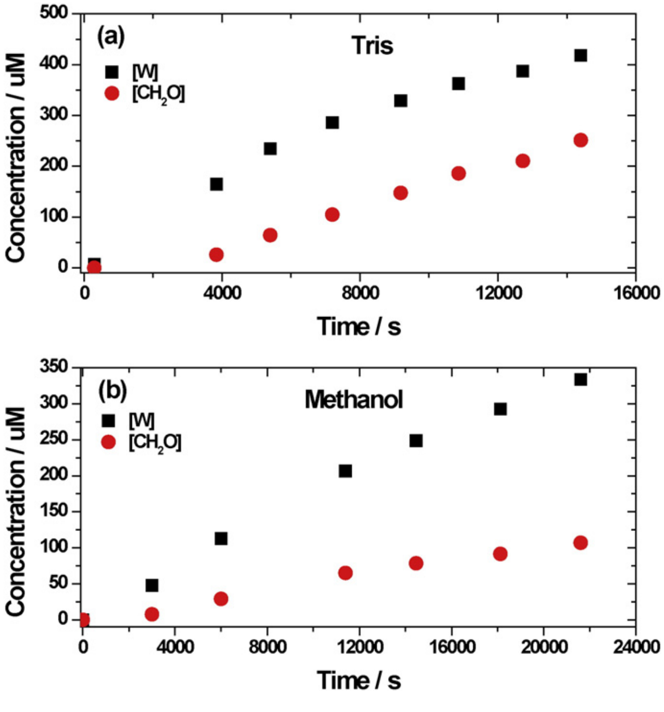

Fig. 1. Concentration of dissolved tungsten ([W], used through the whole paper) (black squares) and CH_2O (red circles) as a function of reaction time in aerobic solutions: (a) Tris (100 mM, pH 7.5) and (b) methanol (100 mM, unadjusted pH).