The Effect of •OH Scavenger on the Formation of Cobalt Oxide Nanoparticles by Gamma-Radiolysis

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Summary

Gamma irradiation of an aqueous solution initially containing 0.1 mM Co^{II} led to the formation of uniform-sized nanoparticles in the range of 10-20 nm. The particles were characterized using Raman spectroscopy and found to be composed of Co_3O_4. Addition of *tert*-butanol (an •OH scavenger) was found to be very effective in suppressing the oxidation of Co^{II} and the formation of cobalt oxide particles.

1. Introduction

One of the issues for nuclear power plants is materials performance in radiation environments. Corrosion of piping can lead to the release of dissolved metallic ions (such as cobalt, iron and chromium) into the coolant that gets transported through the reactor core. The dissolved metal ions, once transported to the reactor core, can be neutron activated and become radioactive. If the radioactive material is re-suspended into the coolant and deposited outside of the biological shield of the reactor core, it can pose a radiological hazard to maintenance workers [1]. This is a particularly important issue posed by the formation of ^{60}Co. On-line coolant purification systems are used to remove dissolved ions and particulates, but their efficacy depends on the size of the particulates that are present; they are often not effective for removing colloids or particulates with sizes less than 0.1 μm. Hence, understanding the mechanisms for formation of very small cobalt particulates is important.

Water, when exposed to ionizing radiation, decomposes to yield a number of chemically reactive species. These water radiolysis products are highly redox active and include both oxidizing (e.g., •OH, H_2O_2 and O_2) and reducing (e.g., •H, $•e_{aq}^-$ and $•O_2^-$) species [2, 3]. These species can readily interact with dissolved metal ions and change their oxidation states. Since the solubility of a transition metal ion can vary by several orders of magnitude depending on the oxidation state of the metal ion, reactions that can alter this oxidation state are important in controlling the concentrations of metal ions in solution and their condensation to form solid particles.

In previous work, we have found that dilute (0.2-0.3 mM) Co^{II} solutions will form nano-scale Co_3O_4 particles when exposed to γ-irradiation [4]. The process of particle formation includes the adsorption of Co^{II} on nucleates and rapid oxidation of the Co^{II} to CoOOH by the oxidizing radiolysis products, •OH and H_2O_2. The mechanism of particle formation is explained in more details elsewhere [4].

Since the particle formation process involves an oxidation reaction, we decided to further investigate the role that •OH plays in controlling the particle size distribution. To do this, we performed irradiation experiments on cobalt solutions that also contained *tert*-butanol. The *tert*-butanol is widely used as an •OH radical scavenger in aqueous solutions since it produces a relatively stable radical ($\bullet CH_2(CH_3)_2COH$) [5] via reaction with •OH.

$$\bullet OH + (CH_3)_3COH \rightarrow \bullet CH_2(CH_3)_2COH + H_2O \quad (1)$$

2. Experimental

All solutions were freshly prepared from high-purity cobalt (II) sulfate obtained from Sigma-Aldrich (purity ≥ 99%) and *tert*-butanol obtained from Sigma-Aldrich using water purified by a NANOpure Diamond UV ultrapure water system (resistivity of 18.2 MΩ·cm). Tests were performed with 0.1 mM Co^{II} solutions at pH 10.6 by adjusting the pH using a 1 M NaOH solution. Prior to a test, the solution was aerated by purging with high purity air (Praxair) for one hour. Using a syringe, a test solution was transferred to pre-sealed 20-ml vial leaving no headspace. The sample vials were irradiated in a ^{60}Co gamma cell (MDS Nordion) as discussed in detail in previous publications [4, 6]. The gamma source provided a uniform absorption dose rate of 5.5 $kGy \cdot h^{-1}$ in the water samples at the time of this study.

Following irradiation for a desired period of time, small volumes of the test solution were extracted by syringe and the cobalt speciation in the solution was determined. The concentrations of Co^{II} and Co^{III} species (dissolved or dispersed as particles in solution) were determined by reacting a sample with 4-(2-pyridylazo) resorcinol (PAR) to form a coloured complex that absorbs light at 510 nm with a molar extinction coefficient 5.6×10^4 $M^{-1}\cdot cm^{-1}$,as discussed in detail elsewhere [4].

Particles were collected by centrifuging samples of the test solution and drying the collected solid on a glass plate in air. The sizes and shapes of the particles were directly measured using transmission electron microscopy (TEM) with the electron microscope operated at 80 keV. Raman scattering measurements to determine the particle chemical composition were performed using a Renishaw model 2000 Raman Spectrometer with a laser excitation wavelength of 633 nm.

3. Results and Discussion

Prior to irradiation, a 0.1 mM Co^{II} solution, with or without added 1 M *tert*-butanol, was clear and light pink in colour. The solution with added *tert*-butanol did not change colour, even after exposure to γ-radiation for 300 min. The solution without any *tert*-butanol remained clear and the colour changed to brown after 5 min of exposure to γ-radiation. After 10 min of irradiation, some precipitates collected at the bottom of the test vial. The colour change of the solution is due to conversion of the dissolved Co^{II} to hydrated Co^{III} species. This conversion was further confirmed by the solution colorimetric species analyses. The results of those analyses as a function of irradiation time are shown in Figure 1. At pH 10.6, without any *tert*-butanol, the initial Co^{II} was converted to Co^{III}, with the reaction reaching completion after about 150 min. The final Co^{III} concentration is less than the initial Co^{II} concentration. This difference is attributed to the formation of the particulates that were observed in the test.

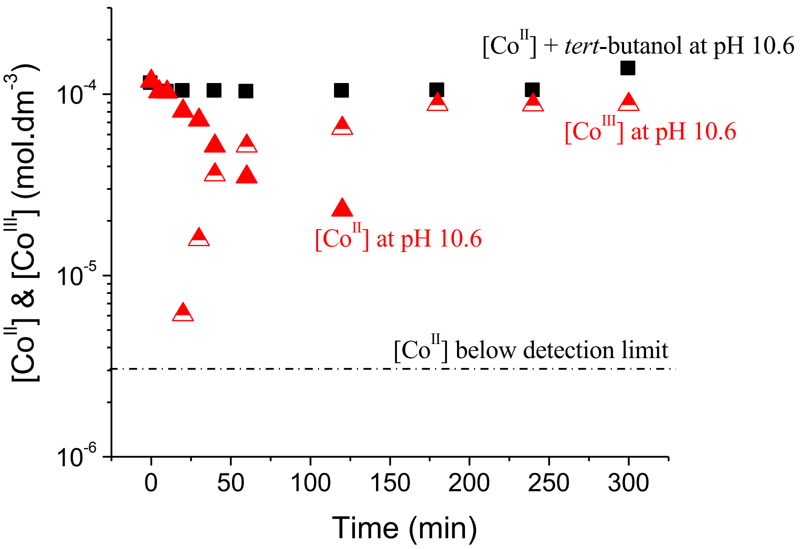

***Figure 1**: Cobalt speciation as a function of irradiation time for 0.1 mM Co^{II} solutions with and without tert-butanol, at pH 10.6.*

Figure 2a shows TEM images of the particles formed in a 0.1 mM Co^{II} solution at pH 10.6 after 300 min of irradiation. For shorter irradiation periods, the particle size distribution was the same, but fewer particles were observed. The final particle size in all cases was 10-20 nm. The Raman spectra of these particles were compared with the spectra of standard samples of various cobalt oxides and hydroxides. It was found that the spectra of the particles were a good match with the spectrum for Co_3O_4, see Figure 2b. There are no unidentified major peaks in the particle spectra indicating that they are essentially pure Co_3O_4.

Our previous studies [7,8] have established that radiation-induced nanoparticle growth requires nucleation sites where the metal ions can be continuously adsorbed and oxidized. For iron and chromium oxide nanoparticles, nucleation sites are formed by homogeneous radiolytic oxidation or reduction of the dissolved metal species (Fe^{II} and Cr^{VI}) to insoluble hydrated species, ($Fe(OH)_3$ and ($CrOOH$) [7,8]. For the cobalt system, the homogeneous radiolytic oxidation of dissolved Co^{II} is slow and $Co(OH)_2$ particles are formed from hydrolysis of Co^{II} followed by condensation to provide the nucleation sites for the nanoparticle growth [4]. For this reason, cobalt nanoparticles are not formed at low pHs where the solubility of $Co(OH)_2$ is high. In the presence of the $Co(OH)_2$ nucleates, radiolytic oxidation can occur more readily. Upon exposure to γ-radiation, the Co^{II} or Co^{II} adsorbed on the particles will be quickly oxidized to CoOOH by •OH and H_2O_2:

$$Co^{II} + \bullet OH \ \ (\text{or } H_2O_2) \rightarrow [Co(OH)_3] \rightarrow CoOOH + H_2O \qquad (2)$$

The CoOOH is relatively insoluble at pH 10.6 [9] and hence, grows as a solid phase on which more Co^{II} can condense. At longer times the CoOOH is converted to the thermodynamically more stable Co_3O_4 by a slow but irreversible dehydration process:

$$2\ CoOOH + Co(OH)_2 \rightarrow Co_3O_4 + 2\ H_2O \qquad (3)$$

The result is particles that are pure Co_3O_4 with a narrow size distribution. Although Co_3O_4 is thermodynamically more stable than CoOOH, direct formation of Co_3O_4 from $Co^{II}(aq)$ is not kinetically favoured.

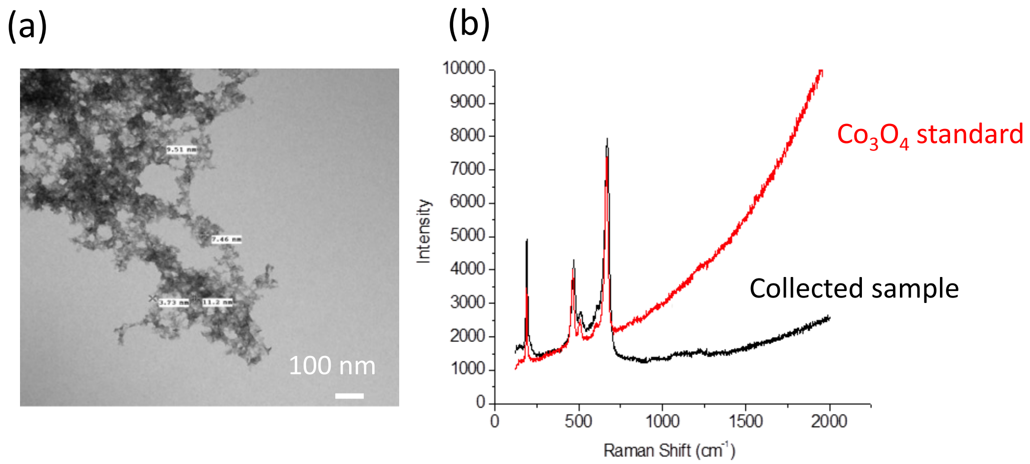

***Figure 2**: (a) TEM images showing the size and morphology of cobalt nanoparticles and (b) Raman spectrum of cobalt nanoparticles formed by the radiolysis of 0.1 mM Co^{II} solution at pH 10.6. The spectrum of standard Co_3O_4 is also shown in (b).*

The Co^{III} in Co_3O_4 can also be reduced back to Co^{II} by the reducing radicals generated by γ-radiation. The two oxidizing and reducing processes lead to the system reaching a steady state quickly as the amount Co_3O_4 present increases. When the steady-state is achieved, there is no further net particle growth. This balance explains the uniform sizes of the cobalt particles that are formed.

In the presence of an •OH scavenger, *tert*-butanol, the concentration of Co^{II} did not change with irradiation time, indicating that no oxidation of Co^{II} to Co^{III} occurred, even after 300 min of irradiation. Consequently, no nanoparticles were observed.

The rate constant of the reaction of *tert*-butanol with •OH (reaction 4) is $6\times10^{8}\ M^{-1}\cdot s^{-1}$ [5]. This is much faster than the rate of the reaction of Co^{II} with •OH ($1.6\times10^{6}\ M^{-1}\cdot s^{-1}$) reaction [10].

$$\bullet OH + (CH_3)_3COH \rightarrow \bullet CH_2(CH_3)_2COH + H_2O \qquad k = 6\times10^{8}\ M^{-1}\cdot s^{-1} \quad (4)$$

$$\bullet OH + Co^{II} \rightarrow Co^{III} + OH \qquad k = 1.6\times10^{6}\ M^{-1}\cdot s^{-1} \quad (5)$$

At the Co^{II} concentration of 0.1 mM and the *tert*-butanol concentration of 1M used in this study, the rate of reaction 4 is 6 orders of magnitude higher than the rate of reaction 5 and is therefore very effective in suppressing the cobalt oxidation.

4. Conclusions

Our study clearly demonstrates that the radiolysis of dilute cobalt solutions can produce highly uniform, nanometer-sized cobalt oxide nano-particles. The addition of oxidizing scavenging agents (like *tert*-butanol) can effectively alter the water radiolysis product concentrations, thereby affecting the cobalt oxide particle formation. To date, we have shown that a high concentration of *tert*-butanol can completely suppress the cobalt oxidation. We are continuing the study of nanoparticle formation at lower *tert*-butanol concentrations to determine whether it is possible to control the size of nanoparticles formed. The effect of hydrated electron ($\bullet e_{aq}^{-}$) scavenger is also being investigated.

5. Acknowledgement

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6. References

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