



Identification of redox states of chemical species on the magnetite surfaces by XPS analysis

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Chromium generally exists as four oxidation states (Cr(0), Cr(II), Cr(III), and Cr(IV)) in natural and engineered environments but two chromium species, trivalent (Cr(III)) and hexavalent (Cr(VI)) forms, are predominant. Cr(VI) is toxic, carcinogenic, and mutagenic, while Cr(III) has been known to be less toxic, immobile, and insoluble in subsurface environments. Chemical speciation of Cr(III) and Cr(II) requiring cutting-edge analytical techniques such as electrospray mass spectrometry is relatively difficult compared to that of Cr(VI). Therefore, most chromium reduction experiments have measured Cr(VI) concentration in aqueous solution using simple colorimetric methods to investigate its reduction to Cr(III), which does not show actual Cr(III) concentration. The redox state of chemical species has been recently identified by advanced surface-sensitive spectroscopic techniques. This research has been conducted to identify the Cr(VI) reduction at the surface of iron oxide (magnetite) by monitoring target chemical species adsorbed on the surfaces and surface sites themselves using XPS analysis. Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks in each spectrum were located at 576.8 ± 0.1 and 586.7 ± 0.1 eV, respectively. The Cr $2p_{3/2}$ binding energies of Cr(III) (hydro)oxides have been reported to be in the range of 576.5 aq 576.9 eV and spin-orbit splitting for Cr(III) between the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ peaks is around 9.9, while the $2p_{3/2}$ peak for Cr(VI) has been done between 579.0 and 579.8 eV and spin-orbit splitting for Cr(VI) is in the range of 8.7 aq 9.4 eV. The spin-orbital splitting of each spectra obtained in this research was 9.9 ± 0.1 eV, therefore we can conclude that Cr(VI) adsorbed on the magnetite surface was completely reduced to Cr(III). Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks are located at 711.2 ± 0.1 and 724.4 ± 0.1 eV, respectively. The binding energy of Fe $2p_{3/2}$ for Fe(II) has been reported to be in the range of 709.0 and

709.6 eV. This indicates that Fe(III) is dominant on the surfaces of magnetite suggesting that Fe(II) on the magnetite surfaces was transformed to Fe(III) by the oxidation with Cr(VI). The intensity of Fe 2p spectra where Cr(VI) was reduced by magnetite was much higher than the intensity of Fe 2p where Cr(VI) was reduced by magnetite with Fe(II) addition. When the same amount of Fe(II) was added to magnetite, which was enough amount to completely reduce initial Cr(VI), the intensities of Fe $2p_{3/2}$ and $2p_{3/1}$ at 200 mg L^{-1} of initial Cr(VI) were lower than those at 50% of the initial Cr(VI). The addition of Fe(II) increased reduction rates by forming the reactive iron complexes and/or precipitates on the surfaces but the intensity of Fe 2p decreased. This may be due to the increase of chromium adsorbed and reduced on the surfaces of magnetite as Fe(II) is added, suggesting that the surface passivation by the chromium complexes and/or precipitates on the magnetite surfaces may significantly affect the intensity of Fe 2p. Based on the experimental results here, we can conclude that the reactive surfaces of magnetite with and without Fe(II) addition reduced Cr(VI) adsorbed on the surfaces to Cr(III) coupled with the oxidation of reactive Fe(II) surfaces to Fe(III). Cr(III) (oxy)hydroxides resulted from the reduction on the reactive Fe(II) surfaces of magnetite seem to overlay the oxidized magnetite surfaces mainly composed of the Fe(III) oxides during the reaction.