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Ligand exchange links adsorption and oxidation of Pt(II) ions on β-MnO_2 surface

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Heavy metal ions are known to adsorb on metal oxides by inner-sphere complex formation and to be followed by reactions such as dissolution of metal oxides and formation of a new solid phase. Among the reactions accompanying to surface complexation, redox of the adsorbed metal ions is one of the most significant phenomena. However, the mechanism of the relation between adsorption and redox is still unclear. Recently Kawamoto et al. (2022) found that Au(III) ion, having average composition of $[AuCl_{1.67}(OH)_{2.33}]$ at pH 4.0, adsorbed on the surface of MnO_2 by inner-sphere complex formation and then reduced to Au(0) [1]. They revealed the ligands around Au(III) was changed from Cl^- to OH^- after the adsorption and prior to the reduction. Assuming that such ligand exchange after inner-sphere complex formation is the key to induce redox reaction, we investigated adsorption of Pt(II) onto MnO_2, which forms also complex with Cl^- and known to be not reduced but oxidized to Pt(IV) after adsorption.

Adsorption experiments were performed with 1.0 g/dm^3 MnO_2 and 0.10 mmol/dm^3 K_2PtCl_4 at pH 4.0 and 25°C. While the experiment, aliquots of the suspension were sampled and filtered with pore size of 0.22 μm. On the other hand, Cl^- and Pt on the filters were analyzed by soaking in 0.10 mol/dm^3 NaOH solution for 24 h, and then washed with 0.10 mol/dm^3 ascorbic acid.

Pt(II) was adsorbed onto MnO_2 immediately and the adsorption ratio reached to 100% after 100 hours. Meanwhile, Pt(II) is supposed to be oxidized to Pt(IV) due to the elution of Mn(II) into the solution was observed. The molar ratio of Cl^-/Pt on the membrane filter tended to decrease with time, suggesting ligand exchange similar to that of Au.

[1] D. Kawamoto, A. Miyazaki, Reduction mechanism of Au(III) species adsorbed on δ-MnO_2, Colloids Surfaces A, 642 (2022)