

Arsenic concentration influences secondary mineral formation during simultaneous As(V) and Fe(III) reduction by *Shewanella* sp.

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Microbial reduction of As (V) and Fe (III)-oxyhydroxides largely controls the solubility and mobility of As in soils and natural waters. Under most conditions, As (III) is sorbed less strongly to oxide mineral surfaces than is As (V), and changes in specific surface area and reactivity resulting from reductive Fe-mineral transformations also influence the sorption of As.

The extent of simultaneous microbial reduction of Fe (III) in ferrihydrite and sorbed As (V), as well as secondary Fe-mineral formation, were studied in batch cultures (serum bottles). Ferrihydrite suspensions (2 g L⁻¹) containing 20, 200 or 2000 μM As (V) and 20 mM lactate in mineral medium were incubated for 38 days in the presence of *Shewanella* sp. ANA-3 under anoxic conditions at 25°C. Iron mineral transformations were monitored by Fe K-edge EXAFS (extended X-ray absorption fine structure) and ⁵⁷Fe Mössbauer spectroscopies.

Increasing As concentrations resulted in an increase in the percentage of As (V) reduced during 38 days (from 40 to 90%). The average As (V) reduction rate increased from 0.24 to 86 μmol As L⁻¹ d⁻¹. The concentrations of dissolved As, mainly As (III), also increased with time up to 80 μM at the higher As concentration, whereas no dissolved As was detected in suspensions containing 20 μM As. The average Fe reduction rate decreased from 32 to 26 mmol Fe L⁻¹ d⁻¹ with increasing total As concentration, while the dissolved Fe (II) concentration decreased by 50%. EXAFS and Mössbauer spectra revealed that mainly magnetite was formed in the presence of 20 μM As, while chloride green rust was identified as the dominating secondary mineral in the presence of 2000 μM As.

In conclusion, the presence of a high As concentration (molar ratio As/Fe~0.1) resulted in an increased As (V) reduction rate, a decreased Fe reduction rate, and inhibited magnetite formation in favor of formation of chloride green rust.

Reactivity of chemically modified nanodisperse anatase

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Titanium minerals are the most important source of titanium, a strategic metal of modern industry. They act in natural and technological processes as interacting substances, homogeneous and heterogeneous catalysts coated on surface of support and consisting of relatively small particles of metal or metal oxides (1–2 nm). Mechanism of nucleation and growth of minerals on nanoscale as well as nonautonomous phases on mineral surfaces could be studied using synthetic analogues of titanium minerals as research model.

Three different TiO₂ have been used as support of Au-systems: commercial Aldrich Titanium (IV) oxide, nanopowder, 99.7 %, anatase and two nanotube-structured TiO₂ with different pH and geometrical parameters. Nonautonomous phases were deposited on the surface of supports by means of a liquid dispensing robot. Chemical reactivity of prepared samples were tested in reaction of preferential oxidation of carbon monoxide. In temperature programmed reactions (TPR) conversion of CO and O₂ as well as selectivity of O₂ towards CO has been determined as a function of temperature.

As CO conversion over the Au-only sample is very low, the selectivity of this system is much smaller, than that obtained over the modified multicomponent systems. Hence, the main role of the modifiers in case of catalysts supported on commercial TiO₂ and titanium dioxide nanotubes is the enhancement of the selectivity. On the bases of previous studies it is very probable that Pb is alloyed with Au, which is main reason for the selectivity enhancement [1]. The bimetallic Au-Pb particle suppresses adsorption of hydrogen; therefore oxidation of CO obtains higher probability.

Addition of Sm can change the nanoenvironment of Au in such a way that it stabilizes dispersion of gold during the reaction, as well as the interfaces between the Au nanoparticles and Sm₂O₃ can facilitate oxygen adsorption. Moreover, due to the atomic contact between oxide modifiers and gold the formation of metal ion – gold nanocluster ensemble sites can activate CO oxidation over the multicomponent catalysts. All these effects contribute to the enhancement of CO oxidation rate.

[1] Tompos *et al.* (2009) *J. Catal.* **266**, 207–217.