

Size matters in crucial redox reactions

October 12 2010

(PhysOrg.com) -- Particle size has a far more dramatic impact on chemical reactivity than previously thought, according to new research from UC Davis. The results have implications for understanding a wide range of vital chemical reactions, from rusting iron to the origins of life.

The researchers, led by Professor Alexandra Navrotsky, studied the energy changes involved in oxidation and reduction reactions in oxides of [transition metals](#). The results were published Oct. 8 in the journal *Science*.

"Oxidation and reduction reactions are the energy source for most chemistry in nature," said Navrotsky, who directs the Nanomaterials in the Environment, Agriculture and Technology program at UC Davis.

Metals such as iron, manganese, cobalt and nickel can combine with different numbers of [oxygen atoms](#) to form compounds with different "oxidation states" and properties. Different crystal structures correspond to different oxidation states: metals in the lowest [oxidation state](#); an intermediate structure called a spinel; and rock salt oxides at the highest levels of oxidation.

Using very accurate measurement of the energy changes involved in changing from one oxidation state to another, Navrotsky's team made two major discoveries about the relationship between the size of particles and their behavior in oxidation and reduction reactions.

First, they found that the energy of oxidation varies dramatically with

particle size, Navrotsky said. Materials made of nanoparticles measured in billionths of an inch behaved quite differently from bulk materials.

"This had not been predicted, nor been thought about before," she said.

The second major finding by Navrotsky's team was that in general, very small particles formed with a lower energy cost for a given metal in the spinel structure compared to other states. That is because the surface energy of the crystal is lowest in the spinel form, allowing smaller particles to form, Navrotsky said.

Because metal oxides are so widespread, the discoveries have wide implications, Navrotsky said. For example, they explain why nanoparticles of wustite, an iron compound, oxidize in exactly the right way to make the heads that read hard disks. They also could lead to new ways to make materials for energy storage or catalysis, and to new understandings of the chemical reactions that powered the first life on Earth.

Navrotsky's co-authors on the study were graduate students Chengcheng Ma and Nancy Birkner and postdoctoral researcher Kristina Lilova.

Provided by UC Davis

Citation: Size matters in crucial redox reactions (2010, October 12) retrieved 19 April 2024 from <https://phys.org/news/2010-10-size-crucial-redox-reactions.html>

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