

Correlation of predicted and measured iron oxidation states in mixed iron oxides

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High-surface-area iron catalysts for catalytic reactions, such as ammonia synthesis, are fabricated by controlled reduction of iron oxide precursors, which are prepared by solidifying an Fe-O melt formed by heating magnetite or hematite (to which iron is often added) to >1600 °C. These catalysts contain a mixture of crystalline magnetite (Fe_3O_4) and poorly crystalline or amorphous wüstite (Fe_{1-x}O with $x \sim 0.05$). A key factor in preparing high-surface-area irons is reportedly the composition of the iron oxide precursor [1]. Pure magnetite precursors yield iron catalysts with appreciably lower surface area and activity than mixtures of magnetite and wüstite. The present study describes work in-progress on measuring variations in the average Fe oxidation state of iron oxide catalyst precursors.

The magnetite and wüstite lattices are both derived from a cubic crystal lattice of oxygen anions. In Fe_3O_4 , one-third of the iron atoms are on interstitial octahedral sites as Fe^{3+} , and two-thirds are on tetrahedral sites, where they exchange their valence between the +2 and +3 oxidation states. In the idealized stoichiometric "FeO" structure, Fe^{2+} ions sit on octahedral sites, while in the actual Fe_{1-x}O structure, some of these octahedral sites are vacant and charge compensation results from Fe^{3+} on tetrahedral sites. For Fe_2O_3 , oxygen ions form a hexagonal close-packed structure and Fe^{3+} cations are located on octahedral sites. Fe cations on tetrahedral sites contribute to a pre-edge feature in the iron K-edge spectra associated with the $1s \rightarrow 3d$. A shift in edge

position of 4.61 eV from Fe_{1-x}O to Fe_2O_3 results from a decrease in average electric charge at the Fe cations of about 0.10.

The present studies were performed on pure iron oxides with the following formal average Fe oxidation states: hematite [+3.00], magnetite [+2.67], and wüstite [+2.11]. Magnetite-wüstite and magnetite-hematite mixtures were prepared to give materials with average Fe oxidation states of 2.24, 2.42, 2.54, 2.80, and 2.89. The measured XAS spectra were normalized by fitting the pre-edge and post-edge regions with first- and third-order polynomials, respectively. The average Fe oxidation states of the mixtures were calculated from the normalized, background-corrected spectra by curve fitting with linear combinations of spectra from the pure components and by interpolating to find the energy at which the edge amplitude reached 0.25 (see Figure 1). The agreement between measured and expected iron oxidation states was within ± 0.04 and ± 0.02 for the two methods, respectively. The extension of the technique to mixed valence iron oxide catalyst precursors is straightforward.

Reference

- [1] R. Schlögl, in *Catalytic Ammonia Synthesis – Fundamentals and Practice*, J. R. Jennings, ed. (Plenum Press, New York, 1991) pp. 19-108.

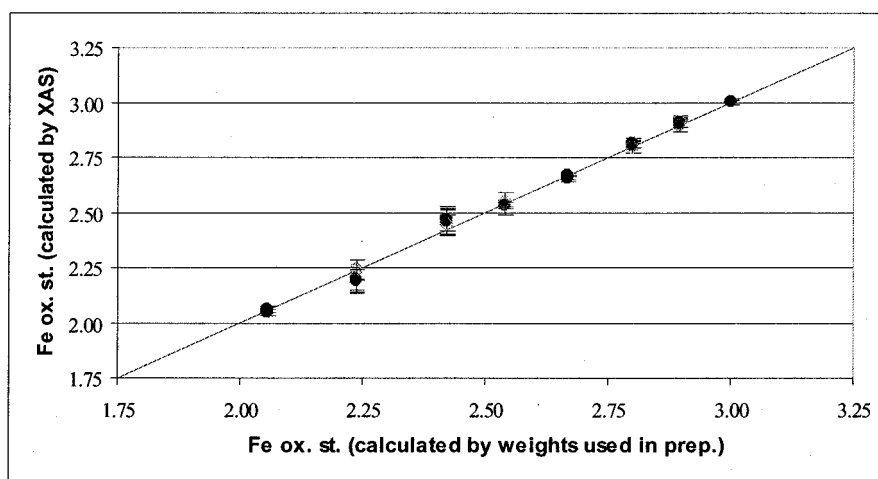


Figure 1: The average Fe oxidation states of the mixtures were calculated from the normalized, background-corrected spectra by curve fitting with linear combinations of spectra from the pure components (open circles), and by interpolating to find the energy at which the edge amplitude reached 0.25 (closed circles).