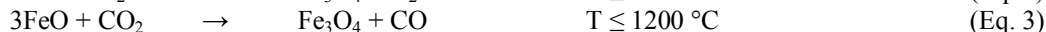
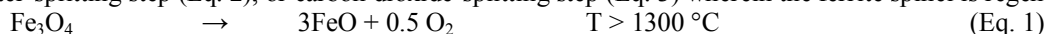


USING IN-SITU TECHNIQUES TO PROBE HIGH TEMPERATURE REACTIONS: THERMOCHEMICAL CYCLES FOR THE PRODUCTION OF SYNTHETIC FUELS FROM CO₂ AND WATER

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In situ X-ray diffraction and thermogravimetric analysis have been employed to probe a ferrite-based solar-thermochemical cycle for the production of CO from CO₂, and H₂ from H₂O. The basic cycle consists of a thermal reduction step (Eq. 1) in which solar thermal energy reduces Fe^{III} to Fe^{II}, *i.e.*, spinel transforms to wüstite, followed by a water-splitting step (Eq. 2), or carbon dioxide-splitting step (Eq. 3) wherein the ferrite spinel is regenerated:



Mixing the ferrites with yttria-stabilized zirconia (YSZ) greatly improves their cyclability, however, this synergistic effect is only partially understood. In order to unravel the underlying mechanisms of the effect and to understand the evolution of thermochemically active phases, we have studied the behavior of iron oxides co-sintered with 8YSZ (8 mol-% Y₂O₃) using in situ X-ray diffraction and thermogravimetric analysis at temperatures up to 1500 °C and under environments representative of those present in a thermochemical cycle. The solubility of iron oxide in 8YSZ measured by XRD at room temperature, following calcination to 1500 °C in air, was 10.6 mol-% Fe. The solubility increased to at least 11.6 mol-% Fe when heated between 800 and 1000 °C under inert (He) atmosphere. Furthermore iron was found to migrate in and out of the 8YSZ phase as the temperature and atmosphere changed, as

evidenced by changes in the 8YSZ cell volume not attributable merely to thermal expansion. In samples containing insoluble iron (*i.e.*, containing > 10.6 mol-% Fe) stepwise heating to 1400 °C under helium caused reduction of Fe₂O₃ (hematite) to Fe₃O₄ (magnetite) to FeO (wüstite). This progression is illustrated in Figure 1 for a physically mixed sample of iron oxide/8YSZ containing 32.4 mol-% Fe pre-calcined at 1450 °C. This gradual thermal reduction from hematite to wüstite was accompanied by evolution of oxygen. The wüstite remained stable upon cooling to room temperature in the helium environment, although after multiple consecutive cycles some of the wüstite was observed to disproportionate to Fe metal and magnetite. Exposure of the wüstite-containing material to CO₂ at 1100 °C enabled re-oxidation of the wüstite to magnetite with evolution of CO. Thermogravimetric analysis allowed quantification of the level to which samples were thermally reduced and were subsequently re-oxidized under CO₂ during thermochemical cycling. Materials with iron oxide contents between 2.0 and 32.4 mol-% Fe in 8YSZ were investigated, and samples with mostly dissolved iron were found to utilize a greater proportion of the iron atoms present than did samples possessing a significant fraction of undissolved iron oxides.

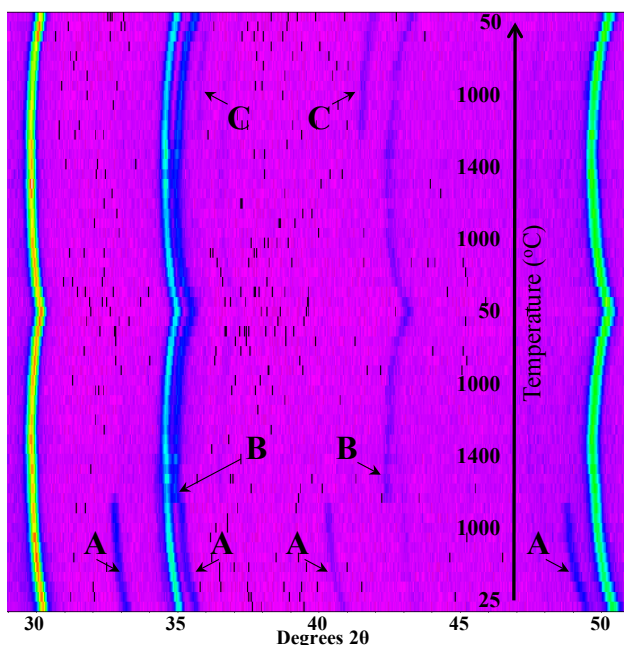


Figure 1. HT-XRD intensity plot for 32.4 mol-% Fe in 8YSZ, cycled two times to 1400 °C under He. Intensities plotted on a square-root scale. A = Fe₂O₃; B = Fe₃O₄; C = FeO; un-marked peaks = iron-doped 8YSZ. Magenta/violet = low intensity; green/orange = high intensity.

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