Study of Ferrous Sulfate Oxidation Under Extreme Conditions Using X-Ray Absorption Spectroscopy

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Abstract

The purpose of this experiment is to analyze how various factors affect the rate of the oxidation of ferrous sulfate into ferric sulfate in iron supplements. The experiment will involve exposing iron supplement samples to atmospheric gases and heat over varying lengths of time. This is expected to reveal the extent to which exposure to heat and atmospheric gases affect the oxidation rate of ferrous sulfate.

The experiment will utilize the APS by employing the XANES and EXAFS methods [1]. X-ray absorption spectroscopy will produce data that shows the oxidation state of the present iron along with the local coordination environment. The results are anticipated to show an increase in the amount of Fe\(^{3+}\) present in the samples exposed to heat and atmospheric gases when compared to a control. [2]

Motivation

Iron deficiency anemia afflicts nearly 25% of the global population; the supplements used to treat this condition lose their potency as they expire. Iron supplements combat anemia by delivering iron II to the body within the compound FeSO\(_4\). The supplements expire when iron II oxidizes to iron III; iron III will pass through the body unabsorbed and the patient will not have received their proper dosage. The expiration of iron supplements poses a less significant issue to citizens of first world countries, who enjoy relatively convenient and inexpensive access to fresh medicine. Conversely, for citizens of third world countries, fresh iron supplements may be scarce or inaccessible—therefore, the extension of their shelf-life is of the utmost importance. Through a greater understanding of the factors which hasten the oxidation reaction, consumers and manufacturers will be able to minimize the oxidation of their medicine and ensure that the medicine provides effective treatment.

Experiment

Samples were prepared by crushing iron supplements into a fine powder which was then put into a long crucible. The experimental samples were subjected to air at 60°C for 55 days and another for 20 days to view possible effects of heat and atmospheric gases over time on the composition of the iron supplement.

Untreated supplements, new and expired, were used as controls for comparison. Unaltered fresh iron sulfate, the active ingredient in the iron supplements, was also subjected to X-ray spectroscopy for comparison. All samples were analyzed using the synchrotron at beamline 9 BM at the Fe-K edge. The precision of the XANES and EXAFS methods made it clear which oxidation states were present in each sample, as well as the sample’s local coordination environment.

Results

This graph directly compares the near-edge spectroscopy of fresh supplements to those treated with heat and exposure to atmospheric gases for 55 days. The edge position was almost identical for the two samples, showing an insignificant change in the oxidation states of iron.

The EXAFS graph shows a noticeable difference in the coordination environment surrounding the iron II atoms of the treated samples; this implies that a change occurred not with the iron, but with the bond lengths surrounding the iron.

Conclusions

There was no significant change in oxidation states of iron between fresh and expired supplements. The data also indicates that there was no significant increase in the rate of oxidation of iron in the samples that were heated versus the control. The fresh supplements have a different local coordination environment than the expired supplements. The data indicates a change in the bond lengths between Fe and O, which suggests that this is the true cause of supplement expiration. Contrary to the hypothesis, the expiration of iron supplements appears to be due to changes in the bonding structures surrounding the iron II compound, rather than the oxidation of the iron.

References

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Uncovering Flaws and Failures in Catalytic Converters Using XANES

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Abstract
The purpose of our experiment was to focus on the causes for the failure of catalytic converters to complete the reactions of harmful compounds to less harmful oxides and relatively inert elemental nitrogen. It is hypothesized that the failure is due to one or more of the following causes:
1) The catalyst is being reacted and consequently stripped from the interface of the converter and the exhaust fumes.
2) The catalyst is being rendered ineffective by the accumulation of scale at the exhaust/catalyst interface.
3) The life of the converter is being reduced through uneven wear and formed a gradient pattern throughout the converter and reduced its effectiveness over time.

Results

![Graph showing results]

Sulfur: Sulfur was found more prominently in the old converter as seen by the large blue spike at 2480 eV. Most likely due to sulfur additives in oil.

Zinc: As soon by the spike at 965 eV, Zinc was not present in the new converter, but was present in the old converter. This is most likely due to an additive in fuel.

Iron: Iron was found in various oxidation states in both converters at 7125 eV, but the converters have different forms of iron. The iron in the used converter cannot perform as a sintering agent.

Conclusion
Our data yields several noteworthy conclusions. Zinc and Sulfur can both be found in additives for engine oil, which are used to prevent wear. Sulfur can also be found as an additive to gasoline in oxide and sulfide forms. The cause of the failure is from an outside source. The failure is caused by Zinc and Sulfur compounds, which are present in the old converter and not the new. Iron is used as part of the substrate to keep the catalyst effective (sintering), but when the oxidation state is changed, it cannot do this effectively, and the catalyst begins to lose functionality. Zinc also builds up as a scale, and prevents the exhaust from contacting the catalytic interference. Sulfur is also more present in the failed converter, and interferes with the intended reaction of the catalytic converter. These issues can be mitigated by finding substitutes to prevent anti-wear additives from engine oil.

Motivation
Carbon emissions from vehicles that run on gasoline are a global concern. Some carbon emissions are caused by the burning of gasoline. Catalytic converters are a device that lowers the activation energies of incomplete chemical reactions in exhaust. Due to constant use and the chemical environment that these converters work in, they tend to fail near 100,000 miles of use, even though catalysts should not be consumed during a chemical reaction. After a failure occurs, no barrier between these harmful emissions and the atmosphere exists, thus negatively affecting the environment.

Experiment
The experiment consisted of two catalytic converters of the same make and model, both designed for 2010 Jeep Wagoneers. One suffered heavy wear to the point of failing federal emissions testing and requiring replacement, and the other was unused. The converter’s catalytic interface was sectioned to expose the interfacial surface to the X-ray beams of the APS. Samples were identified by their location within the converter and the proximity of the sample to the reduction and oxidation stages of the catalytic process. The samples were also identified by the type of pollutant present within the sample.

Samples were analyzed with the synchrotron in beamline 9 BM B. This beamline provided energies from 2.1 keV necessary to perform X ray Absorption Near Edge Spectroscopy (XANES) and Extended X Ray Absorption Fine Structure (EXAFS) on a range of elemental K and L3 edges.

XANES fluorescence measurements were used to determine the concentration of specific elements and were graphically compiled to allow comparison of edge locations between the four different sample sources, which revealed potential changes in oxidation state. After XANES, each trial was continued to perform EXAFS, providing information on the local coordination environment; this information included number of neighboring atoms, type of neighboring atoms, and distance between neighboring atoms, all of which can have a significant impact on XANES edge location.

References

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https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2777224/ - reference for EXAFS
**ABSTRACT**

This paper explores how to use energy from the sun to make fuels. The methodologies presented are novel and show promising results. The motivation behind this research is to develop sustainable energy sources for transportation and industry. The methods outlined include the use of photochemical processes to convert sunlight into usable fuel. The conclusions drawn demonstrate the potential of this technology and suggest further research is needed to improve efficiency and scalability. The next steps involve scaling up the processes and testing under various conditions to ensure practicality. The references cited provide a foundation for this work and encourage further exploration of the topic. This research is critical for the development of sustainable energy solutions and the reduction of carbon emissions.