

Strong catalytic activity of iron nanoparticles on the surfaces of reduced olivine



William C. Tucker^a, Abrar H. Quadery^a, Alfons Schulte^a, Richard G. Blair^{a,c,d},
William E. Kaden^a, Patrick K. Schelling^{a,b,*}, Daniel T. Britt^a

^a Department of Physics, University of Central Florida, Orlando, FL 32816-2385, USA

^b Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, FL 32804, USA

^c Cluster for the Rational Design of Catalysts for Energy Applications and Propulsion, University of Central Florida, Orlando, FL 32816, USA

^d Center for Advanced Turbomachinery and Energy Research, University of Central Florida, Orlando, FL 32816, USA

ARTICLE INFO

Article history:

Received 11 January 2017

Revised 15 August 2017

Accepted 22 August 2017

Available online 24 August 2017

ABSTRACT

It is demonstrated that olivine powders heated to subsolidus temperatures in reducing conditions can develop significant concentrations of 10–50 nm diameter Fe nanoparticles on grain surfaces and that these display strong catalytic activity not observed in powders without Fe nanoparticles. Reduced surfaces were exposed to NH₃, CO, and H₂, volatiles that may be present on the surfaces of comet and volatile-rich asteroids. In the case of NH₃ exposure, rapid decomposition was observed. When exposed to a mixture of CO and H₂, significant coking of the mineral surfaces occurred. Analysis of the mineral grains after reaction indicated primarily the presence of graphene or graphitic carbon. The results demonstrate that strong chemical activity can be expected at powders that contain nanophase Fe particles. This suggests space-weathered mineral surfaces may play an important role in the synthesis and processing of organic species. This processing may be part of the weathering processes of volatile-rich but atmosphereless solar-system bodies.

© 2017 Published by Elsevier Inc.

1. Introduction

Research into space weathering has largely been focused towards strengthening the connection between spectral reflectivity measurements and the composition and morphology of mineral grain surfaces. In addition, there have been many efforts to better understand the mechanistic aspects of space weathering. One of the most characteristic and widely-studied aspects of space weathering is the production of nanophase Fe (npFe⁰), which is linked to darkening and reddening of the reflectance spectra, typically seen in lunar materials (Wang et al., 2012), but also noted in returned samples from asteroids (Noguchi et al., 2011) and in simulated space weathering experiments on Fe- and Mg-rich minerals (Kaluna et al., 2016). Yamada et al. showed that olivine will become significantly darker and redder when subjected to laser irradiation (Yamada et al., 1999), and in 2009 Vernazza et al. argued that darkening and reddening can happen on relatively short timescales (10⁴ to 10⁶ years) due to solar wind (Vernazza et al., 2009). Gaffey (2010) supplied a comprehensive overview of the optical properties of asteroids and the moon and provided

evidence that npFe⁰ is common throughout the Solar System. More direct evidence of npFe⁰ has recently been obtained from samples of 25143 Itokawa S-type asteroid (Noguchi et al., 2011). In short, several lines of evidence point towards npFe⁰ as a common feature of space-weathered mineral surfaces.

While there is widespread acceptance of the presence of npFe⁰ on space-weathered surfaces and their optical activity, the chemical activity of exposed npFe⁰ within a planetary science context has not been systematically investigated. The likelihood that mineral grains are involved in chemical reactions in the coma of comets has been hypothesized previously (Anders, 1991; Gibb et al., 2007), but very little is known about how this might occur. The recent Rosetta mission undertaken by the European Space Agency has yielded direct observations of organic matter on the comet 67P/Churyumov-Gerasimenko (Capaccioni et al., 2015; Goesmann et al., 2015; Fray et al., 2016). Gillis-Davis et al. have shown that non-lunar-like spectral changes associated with nanophase and microphase Fe can be induced in asteroidal samples subjected to weathering (Gillis-Davis et al., 2017), while Kaluna et al. have presented evidence that the growth of micron scale carbon rich particles follows the production of npFe⁰ in simulated space weathering experiments on Fe-rich minerals (Kaluna et al., 2016). In this context, it is important to determine the

* Corresponding author.

E-mail address: patrick.schelling@ucf.edu (P.K. Schelling).

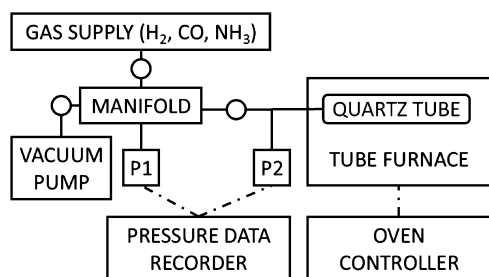


Fig. 1. Schematic of the constructed apparatus used in the experiments. In this schematic, the solid lines between components indicate steel tubing, P1 and P2 indicate pressure transducers for automated pressure recording, and the dashed lines indicate data wiring. The circles indicate the position of valves allowing control of gas flow, permitting isolation of certain parts of the system.

conditions and rates for chemical reactions that can be catalyzed by npFe^0 on mineral grain surfaces, and also how these might vary with the specific composition and morphology of these mineral grain surfaces. There exists an extensive literature devoted towards understanding npFe^0 catalysis at mineral surfaces that can be brought to bear on this issue (Anders, 1991; Hazen and Sverjensky, 2010). It is well known that metallic nanoparticles are strongly catalytic for many reactions. For example, npFe^0 supported on carbon nanotubes has been shown to be strongly active for Fischer–Tropsch reactions (Abbaslou et al., 2009; Bahome et al., 2005; Guczi et al., 2006; Tasfy et al., 2011). Biomass steam gasification also been shown to be catalyzed by an impregnated iron/olivine mixture created by mixing iron nitrate and olivine in solution and utilizing the dried mixture as a catalyst (Rapagn et al., 2011). Based on these previous studies, it seems entirely plausible that space-weathered mineral grain surfaces containing npFe^0 from reduced olivine might demonstrate very strong catalytic activity.

In this paper, we present experimental results demonstrating that olivine samples containing npFe^0 are strongly catalytic for chemical reactions involving NH_3 , CO , and H_2 , all volatiles known to be present in comets and at the surfaces of some volatile-rich asteroids (Gibb et al., 2007; Sandford et al., 2006; Sunshine et al., 2006). Our experimental results show that npFe^0 present on the surfaces of space-weathered minerals can induce dynamical chemical evolution on mineral grain surfaces. At the most fundamental level, npFe^0 acts to catalyze the breaking and formation of chemical bonds. It is hypothesized that npFe^0 could be important for the growth of larger organic molecules from smaller volatiles (e.g. PAHs, NH_3 , CO , and H_2) that are probably found on or near the surfaces of volatile-rich small bodies such as asteroids and comets. Our primary focus is on chemical changes that may occur post-accretion as part of regolith processes of atmosphereless bodies. For this chemistry to occur, reaction feedstocks in the form of volatiles need to be present. In addition to facilitating the growth of larger species, under the right conditions npFe^0 might also act to decompose complex carbon materials known to exist in carbonaceous chondrites (Callahan et al., 2011). This work demonstrates that the characteristic morphology and composition of space-weathered asteroidal regolith results in distinct chemical properties, and provides a new perspective on the importance of space-weathering phenomena.

2. Experimental methods

A schematic of the experimental apparatus is shown in Fig. 1. The manifold was milled from a single block of aluminum, and threads were cut into the manifold to accommodate 1/4" NPT fittings. All tubing connecting the pieces of the apparatus was made

Table 1
Sample descriptions.

Sample ID	Preparation method
A1	250 mg ball milled olivine, sieved
A2	250 mg ball milled olivine, sieved and annealed in air for 1 h at $T = 750^\circ\text{C}$
A3	250 mg ball milled olivine, sieved and annealed in air for 1 h at $T = 750^\circ\text{C}$, then reduced in 10 cycles of H_2 at $T = 500^\circ\text{C}$ for 10 min per cycle, then used to decompose NH_3 at $T = 650^\circ\text{C}$ for 30 min
A4	250 mg ball milled olivine, sieved and annealed in air for 1 h at $T = 750^\circ\text{C}$, then reduced in 10 cycles of H_2 at $T = 500^\circ\text{C}$ for 10 min per cycle, then used to react CO and H_2 at $T = 400^\circ\text{C}$ for 138 h
A5	250 mg ball milled olivine, sieved and annealed in air for 1 h at $T = 750^\circ\text{C}$, then reduced in 10 cycles of H_2 at $T = 500^\circ\text{C}$ for 10 min per cycle, then used to react CO and H_2 at $T = 450^\circ\text{C}$ for 6.33 h
A6	250 mg ball milled olivine, sieved and annealed in air for 1 h at $T = 750^\circ\text{C}$, then reduced in 10 cycles of H_2 at $T = 500^\circ\text{C}$ for 10 min per cycle

of 1/4" 316L stainless steel. Standard Swagelok fittings were used throughout the apparatus. Temperature in the tube furnace was controlled with an Omega CN7853 temperature process controller. SSI Technologies P51 series pressure transducers (model number P51-100-A-A-I36-20MA), which measure pressure against an internal vacuum reference, allowed pressures to be recorded on a computer. The total volume of the system was measured to be 23.8 cm^3 .

For our study, we chose Fo₉₀ San Carlos olivine, which has been studied and characterized extensively. San Carlos olivine is approximately 90% forsterite (Mg_2SiO_4) and 10% fayalite (Fe_2SiO_4) (Fournelle, 2011). To generate surfaces with npFe^0 , the approach in Kohout et al. (2014) was followed in general, but with some variations in the specific details. At each stage of the process, powders used in the reaction were reserved for analysis. A summary of these samples can be found in Table 1. First, approximately 35 g of olivine were ground via high-energy ball-milling in an 8000M SPEX CertiPrep mixer/mill. The milling vial was constructed of tungsten carbide with an approximate volume of 65 ml. Viton flat o-rings were used to maintain a seal during milling. Kinetic energy was supplied for 30 min with three 12.7 mm tungsten carbide balls weighing approximately 16.7 g each. The powders were then sieved through a #325 mesh to produce a fine-grained white powder with a grain size of 44 microns or smaller; a portion of this powder was set aside as sample A1. Milled powder was loaded into the quartz tube with one end open to the ambient air. The system was then heated to $T = 750^\circ\text{C}$ for one hour, and subsequently allowed to cool in air, yielding sample A2. The result of this heating step is the decomposition of the surface material of the olivine grains and the production of nanoscale iron oxide particles. The increase in temperature simulates the energy input from energetic particles such as micrometeorite bombardment. Reaction temperatures were chosen to be substantially under the solidus of olivine but high enough to produce decomposition, reduction, and catalytic reactions in modest time scales. Specifically, this initial temperature $T = 750^\circ\text{C}$ was chosen as it is high enough that the iron within the olivine lattice will become mobile, but it is low enough such that the magnesium or silicon will not become mobile (Barcova et al., 2003; Michel et al., 2013).

To produce npFe^0 , the next step was to reduce the olivine in H_2 . Before introduction of H_2 , the pressure in the quartz tube was reduced to $\sim 0.004\text{ PSIA}$ or lower using a vacuum pump. In contrast to the approach reported in Kohout et al. (2014) which used a flow reactor, in these experiments reduction was achieved by 10 cycles of reduction with H_2 at a pressure of $\sim 20\text{ PSIA}$ H_2 and at a

Download English Version:

<https://daneshyari.com/en/article/5487244>

Download Persian Version:

<https://daneshyari.com/article/5487244>

[Daneshyari.com](https://daneshyari.com)