Oxidation of {100} and {111} surfaces of pyrite: Effects of preparation method

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ABSTRACT

Photoelectron spectroscopy was used to investigate the surface structure and reactivity of two pyrite {100} surfaces, prepared by different means. Specifically, synchrotron-based S 2p photoemission data for a {100} pyrite growth surface prepared by exposure to HCl, and one resulting from mechanical fracture suggested that the acid-washed growth surface showed a higher concentration of elemental sulfur and/or polysulfide impurities. The surfaces, however, showed a similar initial oxidation reactivity under a well-controlled H_2O/O_2 gaseous environment, implying that the fraction of both surfaces that underwent the initial oxidation reaction were similar in structure. The amount of initial oxidation on these surfaces, however, was significantly lower than on an acid-washed {111} growth surface. Photoelectron and ion scattering spectroscopy offer some possible reasons for this structure sensitivity.

INTRODUCTION

Pyrite (FeS₂) has attracted considerable research effort aimed at shedding light on its fundamental surface properties and reactivity. The reason is primarily the importance of the mineral to the environment (Banks et al. 1997). Specifically, pyrite is a mineral commonly found as an impurity in coal, mined by industries worldwide. Exposure of the pyrite to oxidizing conditions during mining leads to degradation of the metal sulfide and eventually the formation of sulfuric acid waste waters. The ramifications of this ecological phenomenon are immense (Pain et al. 1998). It has been argued that a microscopic understanding of the surface reactivity of pyrite, gained with modern surface science techniques, will ultimately lead to new abatement strategies.

One of the important outcomes of prior surface science research has been an appreciation of a strong dependence between the short and long range order of the pyrite surface, and its reactivity toward oxidation. With regard to short range order, prior research has suggested that structural imperfections in a given pyrite crystallographic plane serve as highly reactive sites during the oxidation process (Schaufuss et al. 1998a; Guevremont et al. 1998a). Also, the oxidation rate of pyrite shows a strong dependence on the macroscopic crystallographic plane. For example, the initial oxidation rate of a {111} surface of pyrite is more rapid than a {100} surface (Guevremont et al. 1998b). These results strongly emphasize the need to develop a solid framework for the understanding of the relationship between pyrite structure and oxidation behavior.

The primary motivation here is that different pyrite preparation procedures are commonly used by laboratories when studying the mineral with surface sensitive techniques. For example, the recent research of Schaufuss et al. (1998a) and Guevremont et al. (1998a) addressed the microscopic controls on the initial oxidation reactivity of {100} pyrite samples that were prepared by mechanical cleavage and acid-washing of the natural growth face, respectively. It is important to assess the differences and similarities in the structure and reactivity of the pyrite surface resulting from each preparation method under similar experimental conditions. A comparison will determine the extent to which results and conclusions presented in such types of studies, which have used different pyrite preparation methods, can be used together to develop a microscopic understanding of pyrite reactivity. Toward this end, synchrotron-based photoemission data and initial oxidation reactivity data were used to compare the structure and reactivity of {100} planes prepared by mechanical cleavage and acid-washing of the natural growth surface. The initial oxidation reactivity of these surfaces was also compared to the acid-washed {111} growth surface. A possible reason for differences in reactivity between the {100} and {111} surfaces is presented in view of XPS and ion scattering spectroscopy (ISS) data.

EXPERIMENTAL METHODS

Experimental data presented in this contribution were obtained in separate experimental facilities. The first facility based at Temple University was a combined ultra-high vacuum/high pressure reaction cell. The apparatus is explained in detail elsewhere (Guevremont et al. 1998a) and allowed the mineral samples to be transferred between UHV (10⁻⁹ torr) and environmentally relevant pressures (1 bar). The second experimental apparatus was based at the National Synchrotron Light Source at Brookhaven National Laboratory and was the UHV end-station on the U7a beamline. The end-station was evacu-

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ated to 10^{-9} torr with a turbomolecular and ion pump.

Naturally grown {100} and {111} pyrite surfaces originated from Logrono, Spain, and the Black Sea region of Turkey, respectively. Two procedures were used to prepare the samples for surface science studies. The first method consisted of simple mechanical cleavage of the cubic pyrite sample in a glove bag with a N₂ background. Placement of the cleaved sample into UHV utilized a transfer cell so that the sample was never exposed to the air. The second method consisted of cutting {100} and {111} natural pyrite to produce {100} and {111} growth surfaces. Samples were typically $1 \text{ cm}^2 \times 2 \text{ mm}$ thick. These growth surfaces were then prepared for study by an initial 1 keV He+ ion bombardment in UHV (followed by a 500 K anneal) to remove carbon and oxygen contamination, and subsequent exposure of the samples to 0.5 M HCl for 90 s. The exposure to acid was followed by a rinse with deoxygenated water. The acid rinse removed the outermost surface that was most affected by the bombardment. For the reactivity studies, pyrite was exposed to a gaseous mixture composed of $H_2O(17)$ torr) and O₂ (1 bar) in the reaction cell. All exposures were carried out for 20 h.

XPS data were obtained with MgK α (1253.6 eV) radiation and a double-pass cylindrical mirror analyzer (CMA) at a pass energy of 25 eV. Photoelectron data at the NSLS were obtained with 240 eV photons and a 250 mm hemispherical analyzer (pass energy of 22 eV). Both the cleaved and acid-washed samples analyzed at the NSLS were prepared in an external reaction cell before they were admitted into the UHV chamber. Surfaces were never exposed to the ambient atmosphere.

ISS experiments were performed using a 1 keV He⁺ beam. Reflected ions were energy analyzed by a hemispherical analyzer set to a pass energy of 50 eV. A He⁺-ion scattering angle of 135° was used to obtain all ISS data.

RESULTS AND DISCUSSION

Synchrotron-based S 2p photoemission data were obtained for the cleaved {100} surface and acid-washed growth surface (Fig. 1). S 2p data obtained for the cleaved surface were very similar to those obtained by other laboratories using synchrotron radiation. Spectra were fitted with S 2p peaks at 161.2, 162.1, and 162.7 eV, which have been associated in prior research with S2-, surface shifted disulfide, and near surface disulfide, respectively (Schaufuss et al. 1998a; Bronold et al. 1994). S 2p data of the acid-washed growth surface exhibited these three same features, in roughly the same relative ratios as the spectra from the cleaved sample. In contrast to the cleaved sample, the {100} growth surface exhibited S 2p spectral intensity above ~163 eV (region within the circle in Fig. 1). We suspect, but cannot prove, that this additional spectral intensity results from the presence of some elemental sulfur or polysulfide that forms during the acid-wash treatment. In support of this hypothesis is prior research by Mycroft et al. (1990) that used Raman spectroscopy to identify surface sulfur after pyrite was exposed to acid. Another possibility is that the 163 eV spectral intensity for the acid-washed growth surface could arise from S-O bonds, that form during the acid-wash and subsequent rinse with deoxygenated H2O. While this scenario cannot be ruled out, complimentary XPS measurements on samples



FIGURE 1. Synchrotron-based S 2p data for (**a**) acid-washed {100} growth surface and (**b**) cleaved {100} pyrite. Additional spectral intensity in spectrum (**a**) due to acid-treatment is within circular region. Circles = data points. Light or dotted lines = peaks fit to data. Dotdashed line = baseline. Heavy line = composit of the above. All S 2p data were fit using a 0.65 eV FWHM and a 1.18 eV S $2_{3/2}$ - $2p_{1/2}$ splitting.

prepared in the same manner showed that the relative intensity from oxygen after acid-washing and mechanical cleavage was similar, suggesting that S-O bonds are not the source of the high binding energy peak.

To assess the effect of the differences in surface composition between the cleaved and acid- washed {100} growth surface, initial oxidation reactivity data were obtained for both samples. Specifically, S 2p photoelectron data were individually obtained for the acid-washed {100} growth surface and cleaved $\{100\}$ plane of FeS₂ (Fig. 2), before and after exposure for 20 h to a H₂O/O₂ gaseous mixture. Acid-washed {111} growth surface was treated analogously. Exposure of these three surfaces to the oxidizing mixture resulted in the evolution of a S 2p feature near 168.8 eV (Fig. 2). Consistent with prior research, spectral intensity near 169 eV is assigned to S⁶⁺ of sulfate (Nesbitt et al. 1994). Based on the relative amount of S6+, the cleaved and acid-washed {100} growth surface showed a similar sulfur oxidation reactivity under our experimental conditions. The degree of oxidation was greatest on the {111} growth surface (Guevremont et al. 1998b). Complimentary Fe 2p data (Fig. 3) showed a similar trend in Fe oxidation reactivity. The measure of Fe oxdiation reactivity was taken to be the intensity of the Fe 2p feature at 711 eV, which was probably associated with the presence of Fe³⁺-containing oxide product. These experimental results show that under our experimental conditions the qualitative trend in the relative initial oxidation



FIGURE 2. Pairs of S 2p data, before (top) and after (below) exposure to H_2O/O_2 , for (a) acid-washed {100} growth surface, (b) cleaved {100} pyrite, and (c) acid-washed {111} growth surface.

reactivity between the different surfaces can be inferred from analysis of either the sulfate or Fe³⁺-containing oxide product. The relative rate of sulfate or Fe³⁺ product formation, however, for each individual surface is expected to be different, since recent detailed studies have suggested iron and sulfur oxidation largely occurs independently (Schaufuss et al. 1998b).

Perhaps, the most important experimental observation from the reactivity studies was that the cleaved {100} surface and acid-washed {100} growth surface exhibited similar initial reactivities in an oxidizing H₂O/O₂ gaseous environment. The concentration of surface imperfections have been shown in other laboratories, as well as in ours, to play a significant role in the initial oxidation chemistry of pyrite (Schaufuss et al. 1998a; Guevremont et al. 1998a). Prior research on the cleaved {100} surfaces has suggested that cleavage increases surface concentration of S²⁻, because of separation of the disulfide during mechanical breakage Nesbitt et al. 1998). In contrast, the acidwashed {100} growth surface was first cleaned of impurities in UHV and then exposed to an acid solution. Even though the preparation methods are markedly different, the synchrotronbased S 2p data show that the relative fraction of S^{2-} and S_2^{2-} (i.e., the disulfide) are similar on the two surfaces. Although this similarity might have been unexpected, it does explain why the initial oxidation reactivity of the cleaved {100} surface and acid-washed {100} growth surface are the same (within our experimental resolution). The presence of polysulfide and/or elemental sulfur on the acid-washed {100} growth surface does not appear to affect the reactivity of the pyrite sample. This result suggests that this species resulting from acid-exposure probably decorates the stoichiometric surface. If the polysulfide acted as a site-blocker of surface imperfections (such as



FIGURE 3. Pairs of Fe 2p data, before (bottom) and after (top) exposure to H_2O/O_2 , for (**a**) acid-washed {100} growth surface, (**b**) cleaved {100} pyrite, and (**c**) acid-washed {111} growth surface.

 S^{2-}) that oxidize readily, a significant reduction in the reactivity of the pyrite surface would have been expected.

Concerning the differences in the initial oxidation reactivity of the {100} and {111} surfaces, it is tempting to hypothesize that an increased concentration of Fe^{3+} on the {111} surface is responsible. Such a species is prominent in pyrite oxidation schemes that have recently been proposed (Eggleston et al. 1996; Schaufuss et al. 1998b). Fe 2p XPS of acid-washed {100} and {111} growth surfaces (Fig. 4), within our experimental resolution, does not offer support for such a significant difference in Fe³⁺ concentration in the $\{100\}$ and $\{111\}$ growth surfaces used in this study. More surface sensitive synchrotron-based photoemission of the Fe 2p level, however, are needed to better address any differences. Accessibility of iron in the outermost layer of pyrite to the reactant gas may also be a consideration in understanding the initial oxidation reactivity, since recent studies also have suggested that Fe electronic states on the pyrite surface may control the adsorption of O₂ and H₂O at the initial stages of pyrite oxidation (Rosso et al. 1999). Unfortunately, conventional XPS does not allow the composition of the outermost layer of the $\{111\}$ and $\{100\}$ growth surfaces to be compared due to its rather large sampling depth.

ISS, which is sensitive to the atomic composition of the outermost surface (Niehus et al. 1993), was used to investigate the different pyrite surfaces. While the technique is not well-suited to quantitatively determine Fe:S atomic ratios, it does provide a means to compare relative Fe:S atomic composition on different pyrite crystallographic planes. Representative ISS data are shown in Figure 5. Analysis of three different {111} planes with ISS exhibited an average S:Fe peak-area ratio of



FIGURE 4. Fe 2p XPS data for acid-washed {100} and {111} growth surfaces. The Fe 2p data have been normalized to the total S 2p XPS peak area. The reason for the greater Fe 2p spectral intensity for the {111} surface is not known. It may have to do with differences in the morphology of the acid-washed samples. Regardless of the reason, any difference in Fe³⁺ concentration (intensity within dashed lines) is thought to be small to explain the difference in reactivities of the {100} and {111} growth surfaces.

1.1:1.0 \pm 0.1, and a value of 1.3:1.0 \pm 0.1 was obtained for three acid-washed {100} growth surfaces. The limited sample set makes it difficult to firmly conclude that the {111} growth surface exhibits an enhanced amount of surface Fe relative to the {100} surfaces. These data, however, are not inconsistent with such a contention. Additional studies, particularly ones that use scanning tunneling microscopy, are needed to test this possibility and to explain this structure sensitivity in detail.

In summary, the surface properties controlling the initial oxidation processes on mechanically cleaved {100} pyrite and acidwashed {100} growth surface are similar. This similarity implies that conclusions regarding the fundamental details of pyrite oxidation reactivity published for both types of surfaces are complimentary. Also, while speculative at this point in time, a higher relative number of Fe sites on the outermost {111} growth surface, directly exposed to the reactant, may explain its higher initial oxidation activity relative to the {100} growth surface.

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FIGURE 5. ISS data for an (**a**) acid-washed $\{100\}$ growth surface, and (**b**) acid-washed $\{111\}$ growth surface. The He⁺ scattering peaks associated with reflection from Fe and S are indicated.

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