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Activity of iron pyrite towards low-temperature ammonia production

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ABSTRACT

In this work we report the characteristics of iron pyrite toward the production of ammonia at low temperatures under ultra-high vacuum conditions. We review (with additional unpublished details) our previous systematic study of nitrogen and hydrogen adsorption on single-crystal iron pyrite (FeS_2) and summarise our earlier findings regarding the possibility of ammonia synthesis on this material. We also present new results concerning the adsorption of nitrogen and hydrogen on two related materials, namely molybdenum-treated iron pyrite surfaces and iron pyrite nanostructures deposited on a gold single-crystal. On the bare iron pyrite samples, ammonia is produced upon hydrogenation of preadsorbed N species at 230 K, demonstrating that all hydrogenation steps are possible at low pressures and temperatures. Nitrogen adsorbs molecularly on $FeS_2\{100\}$ at low temperatures, desorbing at 130 K, but does not adsorb dissociatively even at pressures up to 1 bar. Adsorbed nitrogen species can, however, be obtained through exposure to excited nitrogen species. Hydrogen adsorbs on $FeS_2\{100\}$, but only in the presence of an incandescent Ta filament. Recombinative desorption of H_2 occurs at 225 K and is accompanied by desorption of H_2S at 260 K. On the molybdenum-treated iron-pyrite, no appreciable N_{ads} species were detected under the experimental conditions studied, and the same is true for iron pyrite nanostructures on Au{111}. We also provide further details of our efficient and reproducible method for preparing well-ordered stoichiometrically pure $FeS_2\{100\}$ suitable for surface science studies.

1. Introduction

It is estimated that, through the production of large amounts of fertilizers, industrial nitrogen fixation currently sustains the production of food for more than half the human population [1]. The precarious situation of global food supply is likely to be exacerbated by an ever growing global population and the limited uncultivated farmable land remaining (estimated to be 20% of the total) [1–4]. This makes the effective production of ammonia from atmospheric nitrogen arguably the single chemical process for which sizeable progress is most urgently needed [5,6].

Over 150 million metric tons of ammonia are industrially produced every year through the catalytic Haber-Bosch process [2,7]. Despite great efforts in improving this crucial industrial process, the high temperatures and pressures required make it hugely energy-intensive [2]. In a sharp contrast, the enzymatic synthesis of ammonia is carried out under ambient temperature and pressure [8–10]. Intriguingly, while the industrial Haber-Bosch process primarily uses iron-based catalysts, with sulphur being one of the main factors that reduce catalytic activity, efforts in protein crystallography have revealed that the enzymatic active sites (in nitrogenases) are composed of iron sulphide clusters [11]. These nitrogenase catalytic centres are commonly referred to as the Mo-Cofactor, as they present an apex transition metal atom (typically Mo) coordinated to the rest of the cluster, which is believed to influence the adsorption and stability of N_2 [12,13].

Multiple factors contribute to the difficulty of producing ammonia from atmospheric N_2 [14]. First, dissociation of the very strong triple bond of N_2 is recognized as the rate determining step (RDS) in the industrial process. Molecular nitrogen is relatively inert owing to the strength of its triple bond, non-polarity and high ionization potential [15]. Iron is a good catalyst for the dissociative adsorption of N_2, but even so this apparently rate-determining step proceeds at appreciable rates only at elevated temperatures [14]. High temperature is also beneficial in speeding up other steps that may prove rate-limiting, including hydrogenation of surface intermediates and eventual desorption of the product [16,17]. The stoichiometry of the ammonia synthesis reaction, however, implies that high pressures are also then needed to ensure tolerable yield (high temperature favours the reactants as the process is exothermic). As a result the Haber-Bosch process for catalytic synthesis of ammonia

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is estimated to account for consumption of over 1% of the world's annual energy production [2–4].

Several studies suggest that ammonia formation in nitrogenases occurs *via* a non-dissociative mechanism, involving the activation and hydrogenation of molecular $N_{2(ads)}$ species on the surface of the FeS_x cluster [8,11,18]. Moreover, iron sulphide (pyrite) is believed to have played an essential role in the global biogeochemical sulphur cycle, as the reactivity of iron sulphide clusters in nitrogenases and hydrogenases suggest [19]. In consequence iron sulphide is a material of great importance in many environmentally and biologically important reactions [20–23]. Pyrite therefore emerges as an intriguing candidate to study the chemistry of FeS_x centres in biological systems, and towards a possible biomimetic approach for the low-temperature heterogeneous catalytic formation of ammonia. Hence we resolved to study the chemical activity of pyrite towards the species involved in the synthesis of ammonia, and to explore several bioinspired approaches in an attempt to understand the crucial factors that make this material the choice for the natural fixation of atmospheric N_2.

In this article we report a systematic study of the activity of naturally grown pyrite towards the hydrogenation of adsorbed nitrogen species. We review the adsorption of N_2, and H_2 using as-grown $FeS_2\{100\}$ as model material, as well as the formation of ammonia under ultra-high vacuum (UHV) conditions, some of which has been published in detail elsewhere [24,25]. These fundamental steps are the key to evaluate the kinetics of the formation of ammonia, and have been thoroughly studied and debated in the context of the Haber-Bosch process. Initially, ground-breaking work by Gerhard Ertl during the 1970s and 1980s [26–30] suggested that the rate-determining step in the Haber-Bosch process is likely to be the adsorption of nitrogen. However, the dynamics of N_2 dissociative adsorption on Fe surfaces have been revealed to be surprisingly complex, since the low sticking probability of N_2 does not appear to be due to a significant activation barrier to the actual dissociation process, instead arising from a barrier to entry into an unusual molecular precursor state [31]. To further complicate the issue, Strongin and Somorjai [32] have shown that the desorption of ammonia may be effectively rate-limiting under industrial conditions, due to NH_3 blocking of sites for N_2 adsorption. Furthermore we present our efforts to study the influence of the chemical composition (through Mo-doping), and size (through the formation of Fe_xS_y nanoclusters) towards the adsorption of N_2 on iron sulphide. We also discuss a convenient, efficient and reproducible method for preparing well-ordered naturally-occurring $FeS_2\{100\}$, since pyrite surfaces are highly prone to crystallographic disordering, which has a great impact on the reproducibility of studies of their surface reactivity [19,21,33–35].

2. Experimental details

The experimental work was performed in an ultra-high vacuum (UHV) stainless steel chamber (base pressure $< 2 \times 10^{-10}$ mbar), equipped with a 3-grid LEED optics (VG RFA 640), an electron gun (VSW EG10), a concentric hemispherical analyser (VSW HA50), an ion gun (VSW AS10), and a quadrupole mass spectrometer (Hiden HAL201) installed on a retractable linear drive.

Naturally-occurring pyrite single crystals with well-developed {100} habit planes were purchased from Manchester Minerals as $2 \times 2 \times 2\,cm^3$ cubes. The crystals were mechanically machined into $10 \times 8 \times 1\,mm^3$ thin films with one surface left as naturally-grown. The back of the crystal was glued by an Ag silicate paste (Agar Scientific) onto a Ta foil (thickness: 0.05 mm), along the edges of which 0.5 mm Ta wires were spot-welded. These served as structural supports (running parallel along two opposite sides of the crystal film) and intimately sandwich the crystal, and as heating wires. This assembly was then spot-welded to the sample holder. An alumel-chromel thermocouple junction was glued at the back of the crystal using Ag silicate paste for sample temperature measurements. Calibration of our temperature recording system implied a systematic error of less than 10 K, primarily due to degradation of the silicate paste over time, and was corrected accordingly. The sample manipulator can be filled with liquid nitrogen to cool the crystal down to a temperature of 165 K.

As discussed in the next section, an *ex situ* acid pre-treatment was found to be advantageous in greatly reducing the number of sputter/anneal cycles needed to clean the surface *in vacuo*. A typical procedure is as follows: 30 min ultrasonication in isopropanol followed by 30 min in deionized water, and then in 200 ml 1 M HCl solution for 10 min; finally, rinsing and ultrasonication in deionized water. Subsequently the *in vacuo* cleaning procedure consisted in cycles of 200 eV He^+ sputtering (He BIP *plus*, Air Products) followed by 600 K annealing. Since the VSW AS10 ion gun produces an ion beam with a fixed nominal kinetic energy of 500 eV for singly-charged ions with the sample at earth, we applied a positive bias potential to the sample to retard the kinetic energy of positively charged ions. Typically, a single sputtering cycle of less than 30 min was sufficient to reduce all contaminants below the detectable level using Auger spectroscopy. Additional annealing at 600 K for at least an hour was necessary to obtain a sharp (1×1) LEED pattern corresponding to the $FeS_2\{100\}$ surface. Annealing beyond 600 K was avoided to prevent thermal decomposition.

Molybdenum deposition on $FeS_2\{100\}$ was effected by exposing Mo at 170 K using an electron-beam-assisted evaporator (Omicron EFM3) from a rod material (Goodfellow, 1.0 mm, 99.99%) at 910 eV and 40 mA (emission). Mo coverage was controlled by varying the evaporation time, typically 0–25 min, while maintaining a constant evaporation flux (~25 μA). Mo coverage up to 1 ML was estimated by the disappearance of the Auger Fe peak at 50 eV and the absence of the (1×1) LEED pattern corresponding to $FeS_2\{100\}$. Deposition rate was estimated at 0.2 ML/min.

Iron sulphide clusters were produced on a clean Au{111} surface by electron-beam deposition of Fe (Goodfellow, 1.0 mm, 99.99%) under an atmosphere of H_2S (1×10^{-6} mbar) at 400 K, followed by anneal to 673 K (under same pressure of H_2S) for 15 min. Fe exposure was controlled by varying the evaporation time, typically 0–20 min, while maintaining a constant evaporation flux (~15 μA). The amount of Fe and S present on the Au{111} after e-beam deposition was evaluated by AES.

3. FeS_2 single crystal preparation for UHV studies

The preparation of reproducibly well-defined pyrite surfaces has been a challenging issue for detailed surface science studies of this material [33–35]. There are two common methods reported for the preparation of clean pyrite surfaces for studies under UHV conditions: (i) The *in vacuo* cleaving of a pyrite single crystal, and (ii) sputtering a naturally grown single crystal. Both methods have severe limitations; the former produces an essentially clean but macroscopically rough surface, with uncontrollable incidence of defects [36–38], while the latter induces severe surface disorder that cannot be readily removed by annealing, requiring special precautions to mitigate cumulative damage [39,40]. Low-mass sputtering gases with low kinetic energies are therefore normally preferred to clean pyrite surfaces *in vacuo*, such as the use of 200 eV He^+ instead of 500 eV (or more) Ar^+ commonly used for metal surfaces, in order to minimize disordering [39]. The lower kinetic energy used with He^+, however, compromises the sputtering efficiency. Multiple sputtering/annealing cycles are therefore required, and although the damage introduced in a single sputtering cycle is reduced, the overall cumulative damage is not.