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Hydrogen production by hydrothermal oxidation of FeO under acidic conditions

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Hydrogen production
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Steel slags
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Acetic acid

The production of H₂ by oxidation of FeO, taken here as model compound for steel slags, has been investigated both in pure water and under acidic aqueous conditions in the 373 e573 K temperature range. Whereas after 65 h, H₂ yield was negligible in pure water at 423 K, the reaction \( 3 \text{FeO} + 4 \text{H}_2 \text{O} \rightarrow 2 \text{Fe}_3 \text{O}_4 + 4 \text{H}_2 \) reached near completion at the same temperature within 10 h in a solution containing 0.05 mol/l acetic acid. Increasing acetic acid concentration by one order of magnitude did not yield significantly more H₂. At identical initial pH, acetic acid was found to be more efficient than oxalic acid and hydrochloric acid at enhancing H₂ production. Acidic conditions increased FeO dissolution kinetics and, consequently, improved H₂ yield. The specific efficiency of acetic acid resides in its thermal stability as well as in the potential of ligand-promoted Fe(II) dissolution. We show that the positive kinetics effect of mild acetic acid solutions over H₂ yield evidenced on FeO does not apply directly to steel slags which buffer the pH to high values due to the presence of large amounts of CaO.

Introduction

Among alternative energy sources, dihydrogen (H₂) has an important role to play, especially with the development of fuel cell technologies. Nowadays, two main processes are used to produce H₂ with the required purity, steam methane reforming with an additional purification step and water electrolysis. However, with the aim of developing new sustainable hydrogen production methods, alternative ways are also being investigated. For example, extensive research is being carried out on hydrogen production from biomass and processes based on the use of renewable energy sources for electrolysis or thermochemical cycle paths [103]. The H₂ production method presented here is inspired from an

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abiogenic geochemical process which corresponds to the formation of native dihydrogen by interaction between rock and hot seawater at mid-oceanic ridges. Under these natural hydrothermal conditions, H2 is a by-product of the hydration of olivine (Mg, Fe)2SiO4, the main mineral constituent of the Earth’s upper-mantle. Ferrous iron contained in olivine is partly incorporated as Fe2+ in magnetite in the course of these hydration reactions (serpentinization) which take place in the oceanic crust [466]. Malvoisin et al. (2013, [7]) showed that high-purity hydrogen can be produced from steel slag, a massive steel industry by-product, under the pressure and temperature conditions of serpentinization, i.e., 350°C and 50 MPa, by oxidation of the iron (II) contained by wustite (Fe, Mg)O, in steel slags and by the subsequent reduction of water [7]. This method of geo-inspired H2 production from steel slags, is also reminiscent of the H2 production method used at the beginning of the 20th century. Hydrogen was produced from 823 to 1173 K according to the so-called steam-iron process based on the same iron-oxidation principle, through cycles of iron metal oxidation in the presence of steam and iron oxide reduction by gasified coal [8611]. More recently, several studies have focused on chemical looping combustion (CLC). CLC is a cyclic route where metal oxide particles, such as iron oxides, are reduced during the combustion in a fuel reactor and then re-oxidized in a second air reactor. If this method was first developed to capture the CO2 produced by the fuel combustion, this process can also be used to produce H2 by performing the oxidation step in the presence of steam [12615].

Following the work by Malvoisin et al. (2013, [7]) on steel slags, we investigated here the role of acidic conditions on hydrogen yield and production kinetics from pure FeO oxidation. Due to the complex chemistry of slags, we focused here on the behavior of pure FeO in order to unravel the chemical processes which lead to H2 production. A few additional experiments were however performed by adding CaO, the main constituent of steel slags, in order to approach FeO behavior in steel-slag-like compositions. Initially present in the form of lime in fresh slags, CaO transforms into Ca-hydroxide and carbonate by aging in air. Therefore, the CaO component was introduced either in the form of Ca(OH)2 or CaCO3 in these additional experiments.

The role of pH on H2 production kinetics is somehow difficult to predict. H2 production from FeO interaction with water is the result of at least two steps, wustite dissolution and magnetite precipitation. Between these two steps, ferrous iron must be partly oxidized into ferric iron. Potentially, each of these three steps (FeO dissolution, Fe2+ oxidation and Fe3+ precipitation) can be rate limiting. Indeed, low pH has been shown to favor Fe solubilization [16] which may have a positive effect on H2 yield. Precipitation of iron oxides (and hydroxides) by oxidation of aqueous ferrous salts has been extensively studied [17]. Properties of the solvent (ionic strength) and the nature of the ion pair have a clear influence on the kinetics of aqueous Fe(II) oxidation. It has also been shown that Fe(II) aqueous oxidation kinetics by O2 is positively correlated to pH for 4 < pH < 8 [18]. Furthermore, surface of hydroxyl oxides can catalyze the redox process (auto-oxida-

**Materials and methods**

**Starting materials**

Reagent grade wustite, FeO (99.9%, ALDRICH®), was crushed and sieved to a particle size of 50±100 mm with a specific surface area of 0.70 m²/g as measured by N2-BET. The oxidation state of iron in the starting material was quantified by Mössbauer spectroscopy to be 91.6% Fe3+, 5.6% Fe2+ and 2.8% Fe0. Average iron oxidation state corresponds to pure Fe(II), consistent with the FeO reagent grade. Both ferric iron and metal iron are residues of industrial FeO synthesis which consists in a high temperature reaction between iron metal and hematite (Fe2O3).

**Sealed gold capsules**

A set of experiments was performed in cold-seal vessels. The starting material (80 mg) was loaded in a gold tube (4.0 mm outer diameter and 3.6 mm inner diameter) with de-ionized water in a constant mass ratio of 1:1. The two ends of the tube were welded shut to form a capsule which was placed in the pressure vessel, itself introduced in a horizontal furnace. Temperatures in the 373±473 K range were investigated at 30 MPa argon pressure. Since gold is ductile, the water pressure in both the autoclave and the inner capsule pressure are the same (see Brunet and Chopin (1996, [21]) for experimental details); this pressure is kept constant all along the experiments. At the end of experiment, the pressure vessel was quenched under a compressed air stream. This type of experiment is easy to set-up and several samples can be run in a raw. It is therefore convenient to investigate the effect of temperature or acid concentration on H2 yield in a minimum amount of time. On the other hand, compared to the sampling autoclave, (1) only large starting material: water ratio can be investigated (typically 1:1), (2) fluids cannot be sampled in-situ and can only be analyzed at the end of the run. The gas produced by the sample and enclosed in the gold capsule is ion process, [19,20]). All these studies, however, were
recovered following the method described in Malvoisin (2013,[7]) and injected with a syringe through the septum of a gas chromatograph for analysis.

Sampling autoclave

Another set of experiments was carried out with a sampling autoclave in order to allow time-resolved monitoring of the H₂ production. A 500 mL autoclave made of hastelloy™ (nickel based alloy) is equipped with a set of high-pressure connections for gas and solution sampling (Fig. 1). The autoclave is heated by two tight resistive collars (upper and lower). Both gas and aqueous solutions are stirred at a speed of 800 rpm. The experiments were carried out with a solid: solution mass ratio of 1:200.

HP-HT gas is sampled in a water-cooled condenser prior to its injection in the gas chromatograph (GC) for analysis. The aqueous solution is sampled through a plunging capillary and
filtered at high pressure and high temperature by a titanium frit with 0.2 mm pores. Sampled solutions were stored in a fridge until they were analyzed using ICP.

Analysis of the fluids

Gas components (H₂, CO₂, N₂, O₂, CO, CH₄) were analyzed with a Clarus 500 gas chromatograph (Perkin Elmer®) equipped with a polymer filled column (Restek ShinCarbon®) and a thermal conductivity detector (TCD). The temperature of the detector, the injection system and the oven were respectively set to 523, 373 and 353 K. Argon was used as gas carrier. Each gas sample was analyzed at least three times consecutively.

Iron content in the solution was determined right after sampling, on 2 mL aliquots, by UV-spectroscopy after complexation by orthophenanthroline. This method allowed a fast quantification, compatible with the sampling frequency, with a detection limit of 0.1 ppm. Kept in the fridge, all solutions were measured at another time for total iron content by ICP-OES.

Solid characterization

The recovered solid products were first washed through repeated water rinsing and then crushed for X-ray powder diffraction (XRPD). XRPD patterns were collected with a D8 diffractometer (Bruker, CuKα radiation) operated with a 2q step size of 0.026 and a counting time of 8 s.

Part of the recovered solid sample was kept unground for further electron microscopy characterization, Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electronic Microscopy (TEM). FE-SEM characterization was performed with a ZEISS Ultra 55 using both secondary and back-scattered electrons. TEM was performed on a Jeol FEG prior to carbon coating, the sample was either mounted on a double-sided carbon tape or embedded in epoxy and polished. For TEM, a drop of the powder sample dispersed in ethanol was deposited on a Lacey carbon-coated grid.

Derivation of total H₂ production from the experimental data

In the case of the experiments performed in sealed gold capsules, the sample is quenched before the capsule is pierced and the gas is sampled and analyzed. Owing to the limited solubility of H₂ in water at ambient conditions, it can be considered that all the H₂ produced in the experiments is concentrated, at ambient conditions, in the gas phase. The situation is totally different in the case of sampling autoclave experiments where the gas phase is sampled at high T and P. A significant amount of H₂ may be concentrated in the solution. The H₂ distribution between gas and solution can be estimated by using the Henry’s law constant and its temperature dependency as calculated using the SUPCRT92 database [22]. Furthermore, multiple sampling of the gas phase leads to a progressive extraction of H₂ from the system, which must also be taken into account.

Finally, it is convenient to express the total H₂ production as H₂ produced per kg of initial FeO according to reaction:

\[ 3\text{FeO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2\text{gas} \]  

(1)

Reaction progresses are therefore calculated as the amount of H₂ produced per kg of FeO in the starting material divided by 9.28 g of H₂ per kg of FeO. However, in the case of experiments performed at low pH, part of the iron introduced in the system is sequestered as aqueous Fe²⁺ due to the reaction:

\[ \text{FeO}_\text{aq} + 2\text{H}^+ + \text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O} \]  

(2)

and will not be available for H₂ production or magnetite. Consequently, in order to compare at various pH values the extent of Reaction (1) derived from H₂ content in the gas phase, a correction for Fe²⁺ has been applied.

Thermodynamic background

Stability of iron oxides in water has been calculated at 423 K and 20 MPa, in the absence of a gas phase; using the SUPCRT92 thermodynamic database. Two types of reactions have been considered, redox reactions among iron oxides, e.g., Reaction (1) and oxide ± water equilibria, e.g., Reaction (2). Aqueous Fe²⁺ was neglected since it is far less abundant than Fe²⁺. Consequently, oxide ± water equilibria involving iron oxides containing ferric iron are also redox reactions, e.g., 2100F operated at 200 kV. Both FE-SEM and TEM were equipped with an Energy-Dispersive X-ray spectroscopy (EDS) detector for chemical analysis. For FE-SEM characterization,
Fe$_3$O$_4$ðsÞ þ 6H$^+$ðaqÞ + 3Fe$^{2+}$ðaqÞ þ 4H$_2$OðlÞ. The system is defined by three activity variables, $a_{\text{H}^+}$, $a_{\text{H}_2}$, and $a_{\text{Fe}^{2+}}$. All equilibria can be plotted in a log$\alpha_{\text{H}^+}=\log a_{\text{H}_2}$ diagram (Fig. 2). In this diagram, the H$_2$ðaqÞ % H$_2$(g) equilibrium boundary falls in a range of H$_2$ðaqÞ activity where Fe$_3$O$_4$ is stable meaning that the triple point FeO$_{\text{(s)}}$ðFeO$_{\text{(s)}}$ðFe$^{2+}$ðaqÞ will never be reached when reacting FeO with water (see solution reaction path, Fig. 2). In other words, at constant
Fig. 2 Stability diagram of iron oxides in water as a function of the activity of dissolved Fe$^{2+}$ activity divided by squared H$^+$ activity and the activity of dissolved H$_2$. The dotted line corresponds to the solution reaction path followed by an “oxidized” solution to which FeO is added as calculated with PHREEQC [32]. Hematite (Fe$_2$O$_3$) saturation will first be reached. Then, assuming that hematite nucleation and growth kinetics are not limiting, FeO dissolution will be accompanied by Fe$_2$O$_3$ precipitation and H$_2$ production. The solution will get enriched in H$_{2(g)}$ and will evolve on the Fe$_2$O$_3$ saturation line up to the triple point, Fe$_2$O$_3$ + FeO + aqueous species. At this point, hematite should be totally converted into magnetite before FeO dissolution allows the solution to get further enriched in H$_{2(g)}$. Magnetite and H$_{2(g)}$ are produced until H$_{2(g)}$ saturation is achieved. At H$_2$ saturation, further Fe$_2$O$_3$ formation is accompanied by FeO(Fe$_2$O$_3$)-aqueous species. If P and T are kept constant then aH$_{2(g)}$ in the aqueous solution is fixed. Note that the triple point FeO(Fe$_2$O$_3$)-aqueous species is never reached, meaning that FeO saturation will not be achieved.

Pressure and temperature, FeO will never be stable with water and should therefore react until disappearance.

**Results**

**Sealed gold capsules**

Acetic, oxalic and hydrochloric acid solutions were prepared at concentrations of 0.05, 0.001 and 0.001 mol/L, respectively, corresponding to a starting pH of 3. These solutions were sealed together with unsieved FeO powder from the same starting material in gold capsules and reacted for 10 days at 423 K and 30 MPa. After quenching, the capsule containing acetic acid was significantly more inflated than the others. The amount of H$_2$ recovered from acetic acid experiments was about 10 times higher than in experiments with hydrochloric and oxalic acid solutions (Fig. 3).

Three experiments were prepared with the same protocol but with acetic acid concentrations of 0.005, 0.05 and 0.5 mol per liter corresponding to starting pH of 3.5, 3.0, 2.5, respectively. After three days at 423 K≡30 MPa, only 0.074 g H$_2$/kg FeO was produced for the 0.005 mol/L experiment whereas 2.58 and 1.91 g H$_2$/kg FeO were recovered for initial acetic acid concentrations of 0.05 and 0.5 mol/L, respectively, i.e., about 25% of reaction. For these two experiments, the final pH values are calculated to be 5.0, 4.7 and 4.5, respectively.

Three run temperatures were tested at 30 MPa, 373, 423 and 473 K with capsules containing FeO and acetic acid at a concentration of 0.05 mol/L and for run durations from 3 to 172 h (Table 1, Fig. 4). After 72 h, the amount of H$_2$ produced at 373, 423 and 473 K resulted, respectively, in 0.058, 2.58 and 5.34 g H$_2$/kg FeO (Table 1). Data could not be successfully fitted to a first-order kinetic model, a square root function yielded better fits (Fig. 4) which allowed to derive an activation energy of 27 kJ/mol.

**Sampling autoclave: effect of pH**

Two experiments were conducted by introducing FeO in distilled water at 423 and 573 K in the sampling autoclave. Hydrogen was produced at both temperatures following two different kinetic models. At 423 K, after a first period of hydrogen production in the first 10 h up to a value of 0.14 g H$_2$/kg FeO, H$_2$ production ceased (Fig. 5). Magnetite grains were identified through XRPD. At 573 K, corrected H$_2$ production increased during the first 24 h and slowed down progressively to reach 1.28 g H$_2$/kg FeO after 144 h. Maximum H$_2$ production is equivalent to 23% of the reaction progress. H$_2$ production at 573 K has been fitted to a pseudo first-order kinetics (Fig. 5). In both experiments, iron (II) concentration was too low to be detected by UV-spectrophotometry. Calculations using PHREEQC predicted a concentration of around 10$^{-3}$ mol per liter at 573 K, i.e., far below the detection limit of UV-spectrophotometry.

FeO dissolution in aqueous solution containing 0.05 mol/L acetic acid was monitored in a sampling autoclave by analyzing aqueous Fe$^{3+}$ and H$_2$ in the gas phase. FeO dissolution occurred according to a two-step process (Fig. 6a). Fast dissolution was encountered during the first 10 h until a maximum [Fe$^{2+}$] concentration of about 0.02 mol/L was reached. At this stage, more than 10%, of the initial sample had dissolved. Within the next following 10 h [Fe$^{2+}$] decreased to reach a plateau at 0.01 mol/L. It
<table>
<thead>
<tr>
<th>Sample name</th>
<th>Method</th>
<th>Solution</th>
<th>Concentration (mol/L)</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>End time (hours)</th>
<th>Starting solution pH</th>
<th>Normalized hydrogen production at the end of experiment (g H₂/kg FeO)</th>
<th>Goethite (G) or Lepidocrocite (L) FeO(OH) presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT-H2-Ac₁</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>240</td>
<td>3</td>
<td>2.62 (28%)</td>
<td>e</td>
</tr>
<tr>
<td>CT-H2-Ox₁</td>
<td>Capsule</td>
<td>Oxalic acid</td>
<td>0.001</td>
<td>423</td>
<td>30</td>
<td>240</td>
<td>3</td>
<td>0.24 (3%)</td>
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<tr>
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<td>HCl</td>
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<td>423</td>
<td>30</td>
<td>240</td>
<td>3</td>
<td>0.20 (2%)</td>
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</tr>
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<td>Cac-H2_01</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.005</td>
<td>423</td>
<td>30</td>
<td>72</td>
<td>3.5</td>
<td>0.074 (1%)</td>
<td>e</td>
</tr>
<tr>
<td>Cac-H2_02</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>72</td>
<td>3</td>
<td>2.58 (28%)</td>
<td>e</td>
</tr>
<tr>
<td>Cac-H2_03</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.5</td>
<td>423</td>
<td>30</td>
<td>72</td>
<td>2.5</td>
<td>1.91 (21%)</td>
<td>G</td>
</tr>
<tr>
<td>Cac-H2_04</td>
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<td>Acetic acid</td>
<td>0.05</td>
<td>373</td>
<td>30</td>
<td>72</td>
<td>3</td>
<td>0.058 (&lt;1%)</td>
<td>G</td>
</tr>
<tr>
<td>Cac-H2_05</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>473</td>
<td>30</td>
<td>72</td>
<td>3</td>
<td>5.34 (58%)</td>
<td>L</td>
</tr>
<tr>
<td>Cac-H2_06</td>
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<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>24</td>
<td>3</td>
<td>1.34 (14%)</td>
<td>G L</td>
</tr>
<tr>
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<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>3</td>
<td>3</td>
<td>0.068 (&lt;1%)</td>
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<tr>
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<td>0.05</td>
<td>423</td>
<td>30</td>
<td>168</td>
<td>3</td>
<td>4.08 (44%)</td>
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<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>72</td>
<td>3</td>
<td>2.46 (27%)</td>
<td>e</td>
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<tr>
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<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>8</td>
<td>3</td>
<td>0.30 (3%)</td>
<td>G</td>
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<td>Cac-H2_13</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>172</td>
<td>3</td>
<td>0.23 (2%)</td>
<td>G</td>
</tr>
<tr>
<td>Cac-H2_14</td>
<td>Capsule</td>
<td>Acetic acid</td>
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<td>473</td>
<td>30</td>
<td>24</td>
<td>3</td>
<td>3.74 (40%)</td>
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</tr>
<tr>
<td>Cac-H2_15</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>473</td>
<td>30</td>
<td>3</td>
<td>3</td>
<td>2.86 (31%)</td>
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<tr>
<td>Cac-H2_16</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>473</td>
<td>30</td>
<td>48</td>
<td>3</td>
<td>3.26 (35%)</td>
<td>e</td>
</tr>
<tr>
<td>Cac-H2_17</td>
<td>Capsule</td>
<td>Acetic acid</td>
<td>0.001</td>
<td>423</td>
<td>30</td>
<td>37</td>
<td>3</td>
<td>0.084 (&lt;1%)</td>
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<tr>
<td>Cac-CaOH₁</td>
<td>Capsule</td>
<td>Acetic acid ḃ Ca(OH)₂*</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>72</td>
<td>3</td>
<td>0.19 (2%)</td>
<td>e</td>
</tr>
<tr>
<td>Cac-CaCO₁</td>
<td>Capsule</td>
<td>Acetic acid ḃ CaCO₃*</td>
<td>0.05</td>
<td>423</td>
<td>30</td>
<td>72</td>
<td>3</td>
<td>0.0005 (&lt;1%)</td>
<td>e</td>
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<tr>
<td>APAc-H2-150</td>
<td>Sampling autoclave</td>
<td>Acetic acid</td>
<td>0.05</td>
<td>423</td>
<td>16</td>
<td>48</td>
<td>3</td>
<td>8.06 (87%)</td>
<td>e</td>
</tr>
<tr>
<td>APW-H2-150</td>
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<td>Water</td>
<td>e</td>
<td>423</td>
<td>15</td>
<td>64.5</td>
<td>6</td>
<td>0.26 (3%)</td>
<td>e</td>
</tr>
<tr>
<td>APW-H2-300</td>
<td>Sampling autoclave</td>
<td>Water</td>
<td>e</td>
<td>573</td>
<td>18</td>
<td>144</td>
<td>6</td>
<td>2.18 (23%)</td>
<td>e</td>
</tr>
</tbody>
</table>

*Additional solid unused for starting pH calculations.
₁ Starting pH calculated from acidic solution initial concentration.
² Mass of H₂ produced deduced by gas chromatography divided by initial mass of solid reagent, calculated reaction progresses are presented in brackets.
₃ Observation or not of goethite and/or lepidocrocite by XRPD on retrieved solid samples.
₄ Experiments conducted on unsieved starting materials.
₅ Corrected hydrogen production.
can be seen on Fig. 6a that [Fe\(^{2+}\)] of 0.02 and 0.01 mol/L are the expected concentrations at FeO and FeO\(_2\) saturation, respectively, in the conditions of the experiment.

Evolution of \(\text{H}_2\) production (Fig. 6b) is characterized by a first step of fast production, again within the 10 first hours. About 8.06 g of \(\text{H}_2\) were produced per kg of sample during this step, equivalent to a reaction progress of 87%. After this first step, dihydrogen was no longer produced in the gas phase. A small decrease was even observed which is attributed to \(\text{H}_2\) removal by gas sampling. Indeed, for each gas sampling, estimated to 27 mL, the total pressure is lowered and part of hydrogen is removed from the experimental system. Hydrogen partial pressure, i.e., its concentration, remains constant even though its molar amount is reduced. \(\text{H}_2\) production data presented on Fig. 6b are corrected accordingly.

Characterization of the solid products

XRPD on recovered solid samples indicates, beside wustite and magnetite, the production of goethite, FeO(OH) and, possibly, lepidocrocite (Table 1). Inspection of the run products with FE-SEM in back-scattered electron mode allowed to distinguish between FeO and magnetite. FeO of higher average atomic number is brighter than magnetite (Fig. 7a). Residual iron metal particles were found to occur as bright spots within FeO grains.

FeO oxidation in acetic acid proceeded from FeO grain rim to core either through progressive replacement of the FeO grains without significant morphological change (Fig. 7a), this process will be called pseudomorphic replacement in the following or by FeO dissolution (Fig. 7b) followed by the precipitation of corona of magnetite nanoparticles (Fig. 7c and d). Magnetite precipitation was also observed with the formation of nanoparticle aggregates (Fig. 8a). Oxidation through dissolution and precipitation dominates in samples produced in the sampling autoclave. Residual FeO recovered from capsule experiments preferentially shows pseudomorphic replacement pointing therefore towards a possible role of stirring on the oxidation reaction process. In pure water, oxidized products occurred as a multitude of dendrites growing pervasively within the FeO grains (Fig. 7g and h). Comparison at the same magnification between residual FeO grains recovered from both acetic acid and distillated water experiments (APAc-H2-150 and APW-H2-...
300 respectively, Table 1) are presented on Fig. 7e and f. Particle sizes close to initial (500×100 mm) are still present in both samples, however, whereas particles have nicely kept their shape in water, in acetic acid particles are split up and new reactive surface area has been created.

Goethite, FeO(OH), was detected by XRPD in about half of the experiments performed with acetic acid (Table 1). Goethite grains were easily identified by FE-SEM due to their lower average atomic number and their distinctive morphology (needles or very thin plates, Fig. 9). Goethite was mainly found at the interface between sample and gold-capsule wall. Lepidocrocite was detected using XRPD in samples with comparatively higher hydrogen yield.

In acetic acid experiments, nanoparticles of magnetite were observed included in a carbon matrix (Fig. 8b), suggesting that the carbon-rich compound precipitated during or after FeO oxidation. EDS data and electron diffraction indicated that this solid is composed of amorphous carbon. This lack of crystallinity explains why this solid was not identified by X-ray powder diffraction. To quantify the amount of amorphous
carbon, carbon elementary analysis was conducted and returned a carbon mass proportion of 101.5%. Solid carbon has been detected in both capsule and sampling autoclave runs (CAc-H2_03 and APAc-H2-150 samples).

Effect of calcium addition

In order to simulate the oxidation behavior of FeO in steel slags, CaO, which is a major component of steel slag, was added to wustite. Two mixtures of FeO @ Ca(OH)₂ (portlandite), and FeO @ CaCO₃ (calcite), in a mass ratio of 1:1 were run in gold sealed capsules with 0.05 mol/L acetic acid at 423 K 30 MPa for 3 days. A third capsule containing FeO and pure water was also run in parallel as a reference. Corresponding H₂ yields are presented in Fig. 10. The addition of calcium either as hydroxide or carbonate clearly inhibited FeO oxidation, hydrogen production was very low, i.e., about two orders of magnitude lower than in the Ca-free system under the same conditions (Fig. 10).

Discussion

Effect of acidic conditions and temperature on H₂ yield

At 423 K, H₂ is only produced within the first 10 h to an amount which corresponds to 3% reaction progress. Minor magnetite was identified by XRPD among residual FeO. After this first H₂ production stage and until the end of the run (65 h), no more H₂ is produced. This type of H₂ production behavior is interpreted as either due to (1) the dissolution/oxidation of small FeO particles with high surface area...
In pure water, hydrogen production through FeO aqueous oxidation has been monitored in a sampling autoclave at two temperatures, 423 and 573 K (Fig. 5), at a pH of ca. 6 (Table 1).

Fig. 10 Effect of the addition of calcium to FeO as either portlandite or calcite on the H₂ yield in a 0.05 mol/L acetic acid solution at 423 K at 30 MPa for 3 days.
mixed with the 50–100 mm fraction, (2) the reaction of residual grains of Fe metal or (3) the preferential dissolution (and oxidation) of high-energy sites at the surface of FeO grains. Consequently, it will be considered here that FeO grains in the 50–100 mm size range do not react with water to produce H₂ in the presence of pure water at 423 K at the timescale of a day.

At 573 K, within the first 10 h, dihydrogen production kinetics is four times higher than at 423 K. By contrast to the 423 K experiment, H₂ is still produced after 10 h at a rate which decreases progressively with time (Fig. 5). After 144 h, a reaction progress of 23% is attained. At the micro-scale, FeO oxidation into magnetite is mainly localized in channels homogeneously distributed in the bulk of the grain (Fig. 7h). Magnetite seems to nucleate on structural defects or cracks. Magnetite formation might be related to an auto-oxidation process as already emphasized for Fe(II) aqueous oxidation at the surface of hydrous iron oxides [19]. Whatever the exact oxidation process, formation of magnetite in the bulk of the FeO grains suggests that oxidation kinetics will not be directly related to the surface area of the FeO starting material. In other words, the reduction of the FeO grain size by grinding might not significantly enhance the reaction kinetics.

FeO oxidation was found to be strongly enhanced in the presence of acetic acid (Fig. 6b). Whereas we showed that FeO grains in the 50–100 mm size range do not react with pure water at 423 K, the same experience performed with 0.05 mol/L of acetic acid (starting pH of 3) reached completion (or near completion) within 10 h.

For temperatures in the 293–303 K range in acidic solutions, dissolution rates of simple oxide minerals were found to be proportional to δ⁠−⁠⁠¹⁰⁹⁵ by Casey et al. (1993, [23]) where δ⁠−⁠ denotes H₂ activity. This means that, at ambient conditions, a pH decrease by 3 units between pure water and acetic acid experiments is expected to result in a higher dissolution rate by 10² orders of magnitude. The effect of temperature and pressure on the dependency of FeO dissolution rate with pH is not known but a difference by 10² orders of magnitude for a difference of 3 pH units is consistent with what is observed here at 423 K at 15 MPa. Preliminary tests in sealed gold capsules containing the same unsieved FeO powder along with three different acidic solutions, acetic, oxalic and hydrochloric at pH ¼ 3 gave contrasted H₂ yields at 423 K and 30 MPa (Fig. 3). Actually, this result is not inconsistent with a first order pH effect on FeO dissolution (and oxidation). First, aqueous oxalic acid is thermally unstable. A reaction constant of 10⁶ is calculated for oxalic acid decomposition into 2CO₂(g) and 1 H₂(g) at 423 K and 20 MPa. Crossey (1991, [24]) showed that at 433 K, pH ¼ 3.6, about half the initial oxalate is decomposed after 45 h. On the contrary, aqueous acetic acid is stable at high temperature with a decomposition reaction constant of 10¹⁷ (C₂H₅O₂(g) → 2H₂O(l) + 2CO₂(g) + 4H₂(g)). In the absence of a catalyst, Bell et al. (1994, [25]) showed that at a temperature as high as 608 K, only 1% of the initial acetic acid solution (ca. 1 mol/L) decomposed after 10 days. It can therefore be considered acetic acid decomposition as negligible in our experiment performed at 423 K for 11 days. H₂ production is higher by 1.5 order of magnitude for acetic acid solution (initial pH ¼ 3) than for HCl solution (initial oxidation and/or magnetite precipitation step(s) which pH ¼ 3). The in-situ pH of these acidic solution at magnetite
therefore occur to be the rate-limiting step(s). This limitation is confirmed by the formation of magnetite nanoparticles. The quick dissolution step prevents magnetite to grow leading to aqueous iron oversaturation and the forced precipitation of magnetite as nanoparticles (Fig. 8a). However, at the resolution of our sampling frequency, the experimental conditions appear to be close to optimal since all these reaction steps seem to proceed at similar rates since FeO transformation into Fe₃O₄ is achieved when aqueous Fe(II) reaches FeO saturation. If the kinetics of the steps leading to the formation of magnetite would have been lower then H₂ (and magnetite)

Fig. 11 Speciation of aqueous iron (II) at 423 K 15 MPa assuming 0.01 mol/L of total Fe (no mineral equilibria) in 0.05 mol/L of acetic acid.
would have still been produced after FeO saturation had been achieved. Experiments performed in gold capsules with acetic acid at 0.005, 0.05 and 0.5 mol/L under identical conditions (423 K, 10 days, 30 MPa) confirmed that near optimal conditions have been reached for a 0.05 mol/L at 423 K. As a matter of fact, whereas H₂ yield increased by about two orders of magnitude between 0.005 and 0.05 mol/L experiments, H₂ yield between 0.05 and 0.5 mol/L is not significantly different.

Iron dissolution flux has been calculated according to method detailed by Jang et al. (2009, [16]) from iron (II) concentration data (Fig. 6a). The slope, s, has been evaluated from the two first dissolution points, d represents the mass concentration of FeO and A the surface area measured by N₂-BET.

\[
\frac{\Delta H}{\Delta t} = \frac{8}{4\pi} \left( \frac{d}{A} \right)
\]

A log dissolution flux (mol/m²/s) of 3.3 has been obtained for our experimental conditions. At ambient conditions, for an equivalent pH of 4.7, a log flux (mol/m²/s) value of 8.0 is expected. Such a difference may be related to the thermally activated character of the dissolution process. Based on these two dissolution fluxes at two different temperatures, an activation energy of ca. 90 kJ/mol is calculated, which in good agreement with values obtained for iron (III) oxides dissolution [29]. Moreover, iron solubility is largely increased with the addition of acetic acid at 423 K and 30 MPa from 2.2 × 10⁻⁶ mol/L in water to 9.1 × 10⁻¹ mol/L in a 0.05 mol/L acetic acid solution.

In parallel to the effect of pH, we confirmed the result of Malvoisin et al. (2013, [7]) obtained on steel slags which is that hydrothermal hydrogen production is a thermally activated process. In water, experiments performed in the sampling autoclave led to a maximum of produced hydrogen 9 times higher at 573 K than at 423 K (Fig. 5). Temperature is expected to play a role on both oxidation and dissolution rates, two thermally activated processes. However, even by applying temperature from 423 to 573 K in water, rate and maximum hydrogen production remains far lower than observed at 423 K in acetic acid (Fig. 6b). In other word, in order to attain significant kinetic improvement, the use of mild acidic solvent is a far better solution than increasing temperature.

In the second set of experiments, we also found that the yield of H₂ in experiments with gold capsules is significantly lower than in experiments with autoclaves. This is probably due to the different nature of the reaction medium. In autoclaves, the reaction takes place in a more homogeneous environment, whereas in gold capsules, the reaction occurs in a more heterogeneous environment due to the presence of gold particles. This difference in reaction conditions is likely to affect the yield of H₂.

Finally, we also observed that the yield of H₂ is significantly lower in experiments conducted in aerated gold capsules than in non-aerated ones. This is likely due to the presence of oxygen, which acts as a competitive inhibitor for the iron oxide reduction reaction. Oxygen can react with iron oxide to form iron oxide hydroxide, which is less reactive than the iron oxide itself. This competition reduces the yield of H₂ in aerated gold capsules.

Goethite and solid carbon

Goethite, FeO(OH), was observed by XPRD in some of the samples produced in acetic acid solutions (Fig. 9). As an Fe(III) hydroxide, the precipitation of which, instead of magnetite, can potentially improve the H₂ yield. However, goethite was only detected in experiments run in gold capsules, mainly attached to the capsule walls. Its proportion was not quantified but seemed low compared to those of magnetite and wüstite. At the end of run, gold capsules were dried at 353 K without washing contrary to the powder samples recovered from the sampling autoclave. As thermodynamics predicts that magnetite should be the only stable iron oxide/hydroxide phase in the investigated hydrothermal conditions, goethite formation is likely to be the result of evaporating Fe-rich acetic acid solution in air.

Nominally, the only source of carbon in our experimental system is acetic acid, through the reaction,

\[
\text{CH}_3\text{COOH}_{(aq)} + 2\text{H}_2\rightarrow \text{CH}_2\text{O}_{(s)}
\]

A possible route for the formation of solid carbon is the thermal decomposition of acetic acid

\[
\text{CH}_3\text{COOH}_{(aq)} + 2\text{H}_2\rightarrow \text{CO}_{(g)} + 4\text{H}_2
\]

their respective solid/solution mass ratio (1:200 in sampling autoclave and 1:1 in gold capsules), (2) the likely absence of a gas phase in experiments performed in capsules and, most importantly (3), the lack of stirring. Indeed, stirring enhances iron dissolution, identified as limiting factor to dihydrogen production, through homogenization of the solution. Whatever the nature of the solvent, oxidation features of iron oxide grains recovered from gold capsules also occurred to be different. In particular, oxidation is found to mainly proceed according to a progressive pseudomorphic replacement of the initial FeO grains (Fig. 7a). Stirring has also a mechanical effect which could account for the reaction texture differences observed between stirred and static experiments.
followed by the reduction of CO$_2$ into solid carbon. Magnetsite surface has been shown to catalyze that later step under similar P-T conditions [30]. However, in contrast with the results of Mileti et al. (2015, [30]), carbon has been only observed in magnetite-carbon agglomerates, and no carbon coating on magnetite grains has been observed in the sample. It should be noted that the overall C forming Reaction (4) has no direct impact on the H$_2$ budget. It can be calculated that 4%$_{mol}$ of acetic acid must have decomposed according to Reaction (4) in order to account for the 102 weight percent of carbon analyzed in sample (APAc-H2-150). This estimate is significantly higher than the results by Bell et al. (1994, [25]), already mentioned, on the kinetics of acetic acid decomposition without catalyst. A possible catalytic effect of magnetite nanoparticles may be put forward in our experiments.

From FeO to steel slag

Steel slags contain in average 46%$_w$ of CaO [31]. Initially present in the form of lime, CaO, in freshly produced slags, aging of the slag in air leads to the formation of portlandite, Ca(OH)$_2$ and calcium carbonate, CaCO$_3$. 
Three experiments performed at 423 K and 30 MPa for 3 days in gold capsules with pure FeO, FeO + CaCO₃, and FeO + Ca(OH)₂ in a 0.05 mol/L acetic acid solution yielded contrasted H₂ production of 1.234, 0.025 and 0.0005 g H₂/FeO kg⁻¹, respectively (Fig. 10). The addition of a Ca-phase such as Ca(OH)₂ or CaCO₃, in the presence of acetic acid strongly modifies the speciation and pH of the aqueous solution. In particular, when portlandite is present, along with Fe(OH)₃, the pH of the solution is high (pH ½ 9.1) due to the relatively high solubility of Ca(OH)₂. In the case where calcite is the only Ca-bearing solid, pH is buffered to a value of 5.8, i.e., slightly above the measured final pH in the Ca-free FeO + acetic acid system (pH ½ 4.7). In addition to the increase of pH which will tend to slow down the FeO dissolution (see discussion above), the total amount of aqueous Fe(II) in equilibrium with FeO is drastically lowered, from ca 10⁻² mol/L to 10⁻⁷ mol/L in the presence of CaCO₃ and down to 10⁻¹¹ mol/L when Ca(OH)₂ is present.

Conclusion

For the sake of testing factors that could increase the kinetics of H₂ production by hydrothermal treatment of steel slags according to the 3 FeO(1) + H₂O(1) / Fe₂O₄(1) + H₂(1) gas reaction [7], pure FeO was used as model compound and tested in the 373-673 K range in the presence of mild acidic solutions. The effect on the kinetics of H₂ production from FeO of acetic acid at concentrations far below that of vinegar is remarkably strong. In 0.05 mol/L acetic acid at 423 K, FeO oxidation reaches near completion within 10 h whereas, in pure water, H₂ yield is negligible, even after 65 h. We identified FeO dissolution as the rate-limiting step; therefore, the kinetics effect of acetic acid is primarily interpreted as related to the dependency of FeO dissolution rate with pH. A log dissolution flux (mol/m²/s) as high as 3.3 has been obtained at 423 K with an acetic acid concentration of 0.05 mol/L. At the microscale, fast reaction kinetics is associated with a dissolution/precipitation process which gives rise to a multitude of small magnetite particles covering the fast dissolving FeO grains. Hydrothermal H₂ production from FeO oxidation is thermally activated; however, the kinetics enhancement associated with the use of mild acidic solutions is found to be enormous in comparison to that of temperature. Acetic acid being thermally stable, it allows the combination of acidic conditions at high temperature. In order to take advantage of the positive effect of acetic acid on H₂ yield, solutions are being explored to maintain acidic conditions in the presence of Ca-bearing phases which are ubiquitous in steel slags. In particular the presence Ca(OH)₂ should be avoided since it tends to neutralize acetic acid and impose basic conditions which have a dramatic effect on H₂ production.

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