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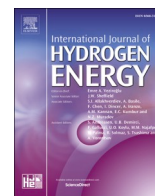
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Demonstration of the co-generation of heat and hydrogen by high-temperature oxidation of aluminum in steam

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ABSTRACT

The development of a circular economy based on the storage of decarbonized energy is essential. A potential solution involves storing surplus (intermittent) green energy by converting metal oxides into metal powders. This is in particular effective in regions with preferred wind conditions and extreme exposure to sunlight. These powders, which can be transported safely, can then be used to release the stored energy as required in other parts of the world. An experimental method involves the oxidation of metal particles in steam to simultaneously generate heat and hydrogen. The first proof of this concept, which shows the full conversion of steam to hydrogen, is presented in this contribution.

1. Introduction

Future storage technologies must be capable of providing all sectors with green energy in the required form such as hydrogen, electricity and heat all-over the year. Concurrently, there is a significant demand for energy storage capacities due to the seasonal variations of local renewable energies, the regional very different availabilities and costs of green electricity, and geopolitical factors like security and resilience. Only carbon-free chemicals such as molecular hydrogen, ammonia and metals from renewable sources are economically viable due to their high storage capacity and the long storage duration required [1]. However, an efficient and cost-effective transport of hydrogen over large distances represents a significant challenge. Metal fuels are emerging as a zero-carbon, high-energy density alternative to fossil fuels due to their availability and recyclability using renewable energies. Aluminum (Al) powder has been primarily investigated in *air/O₂*. Al conversion in water [2–6] or steam is considerably attractive for on-demand co-production of high-temperature heat and hydrogen [7–9]. The ability to alter the form of the released energy from heat to hydrogen by changing the oxidizing agent from oxygen to *H₂O* should also satisfy the anticipated demand for a dynamic energy mix.

There is a need for the development of processes for the continuous oxidation of metals, particularly aluminum, with *H₂O*. Building on recent groundbreaking work that detailed the combustion process of an aluminum particle in pure steam [10], this study offers for the first time experimental proof of the simultaneous production of hydrogen and heat. It also provides details about the combustion products. Since the solid aluminum oxide produced thereby represents a “green” material, there is a keen interest in understanding its physical and chemical properties.

2. Experimental results and discussion

The experimental set-up, as detailed in Ref. [11], features an axisymmetric profiled Bunsen burner designed for the combustion of a custom gaseous mixture containing dispersed aluminum particles.

A methane-rich mixture ($X_{CH_4} = 0.15$) reacts with an oxidizing agent ($X_{Ar} = 0.60, X_{O_2} = 0.25$) to produce gases at high temperature ($T_{eq_CH_4} = 2717\text{ K}$). The composition of the gases produced can be calculated at equilibrium (only concentrations above 2% are indicated): $X_{Ar} = 0.55, X_{H_2O} = 0.23, X_{CO} = 0.08, X_{CO_2} = 0.06, X_{H_2} = 0.04$. Using a methane-rich mixture avoids the presence of oxygen in the hot gases.

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This equilibrium calculation reveals that water vapor is the primary oxidant present. It is important to note that while the oxidizing efficiency of CO_2 is lower than that of water vapor (0.2 and 0.3 respectively), that of CO is 10 times lower than that of water vapor [10]. Hydrogen is present in low concentrations. Aluminum particles, with an average diameter of $7.5 \mu m$ (for more details see Ref. [12]), are transported by the gaseous premix, heated by the methane/oxygen flame and subsequently react with water vapor and carbon dioxide. The methane reacts first with the available oxygen, consuming all of it. The structure of these so-called hybrid flames is described in detail in Refs. [11,13]. The concentration of aluminum particles, set at $500 g/m^3$, is sufficient to reduce all the water vapor to dihydrogen.

The reactive flow is contained and separated from the surrounding air by a quartz cylinder. A stream of argon, smoothed by a porous disc, is blown around the torch (see Fig. 1). A tube with a diameter of $1/8''$ that's connected to a vacuum tank is employed to collect the gases produced at a specific height in the plume of the reactive zone. Sampling begins with the opening of a valve triggered when stable conditions are reached. A submicron filter with a pore diameter of 500 nm is used to capture some of the condensed particles found downstream of the reaction. These powders can then e.g. be analysed by scanning electron microscopy (SEM). The reactive zone can be approximately divided into two sections (from the burner outlet moving downstream): The first section is where methane reacts with all the available oxygen (visible as a slight blue tint), which enables the metal particles to preheat (visible as orange particles). This is followed by a second, highly luminous section where aluminum primarily reacts with water vapor. The estimated temperature of the methane flame ($T_{eq_CH_4} = 2717 \text{ K}$) is higher than the melting temperature of aluminum ($T_{fus_Al} = 994 \text{ K}$) and alumina ($T_{fus_Al_2O_3} = 2345 \text{ K}$), but lower than the evaporation temperature of aluminum ($T_{vap_Al} = 2792 \text{ K}$).

The purpose of this study is to demonstrate for the first time that the high-temperature reaction between water vapor and aluminum can jointly produce i) energy (heat) and ii) hydrogen. The white hue in the reactive zone, visible downstream of the flow in Fig. 1, is a strong sign of considerable release of energy. This energy is split between the sensible heat contained in the two-phase flow and a significant radiative contribution. The white hue is indicative of temperatures reaching at least 3000 K [11].

The sampling tube's height has been adjusted to ensure that its open end is submerged in the area where the reaction between aluminum and

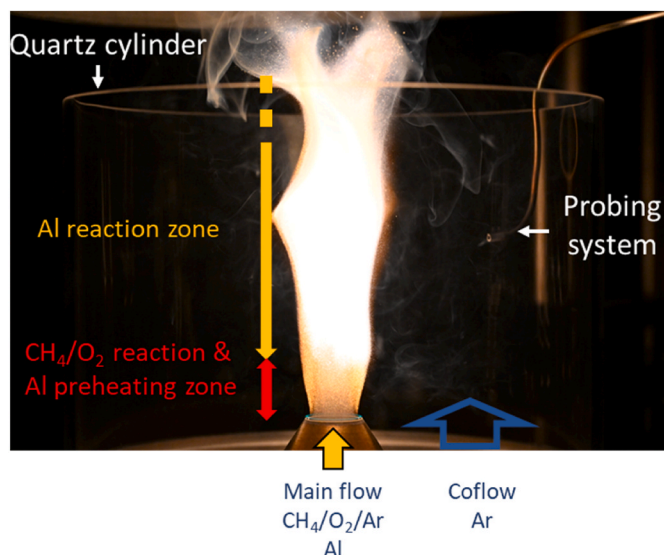


Fig. 1. Sketch of the experimental set-up.

water vapor occurs. Initially positioned away from the reactive zone, the tube's end is shifted into the flame zone to collect a sample once a valve opens, linking the tube to a reservoir that is initially in a vacuum state. The tube's end is rapidly obstructed by condensed particles (excess molten aluminum and alumina), but the suction duration is sufficient to reach about 40 mbar in the 1-L tank. The submicron filter in front of the tank is also clogged at the end of the experiment.

A gas chromatographic analysis (hereinafter referred to as GC) of the sampled gas mixture reveals the following composition: $X_{Ar} = 0.664$, $X_{H_2} = 0.157$, $X_{N_2} = 0.084$, $X_{CO} = 0.069$, $X_{O_2} = 0.084 \pm 0.3\%$

Besides the inert diluent, hydrogen is the dominant gaseous species. The content of water vapor is not measured. These results seem to confirm that much of the water vapor reacted with the aluminum to produce hydrogen. Likewise, all of the carbon dioxide interacted with the aluminum, resulting in its reduction to carbon monoxide. Notice the presence of nitrogen and oxygen. Prior to the experiment, the entire sampling system (tube + filter) was flushed with argon gas. However, it seems that the filter's internal volume was not adequately purged of air. This volume is relatively small (estimated at 0.8 mL), but it is significant considering the tank's end pressure (40 mbar). The ratio $\left(\frac{X_{N_2}}{X_{O_2}}\right)_{GC}$ close to that of air supports this hypothesis. The obtained volume fractions should be compared with those expected when considering the reaction of aluminum with the flue gases produced by the methane flame (equilibrium composition considered): $X_{Ar} = 0.55$, $X_{H_2} = 0.31$, $X_{CO} = 0.14$. The measured mole fraction of argon is higher than expected due to the argon initially present in the tube. The expected ratio $\left(\frac{X_{H_2}}{X_{CO}}\right)_{equil} \sim 2.3$ aligns well with the experimentally measured value, confirming that water vapor and carbon dioxide react with the metal particles.

Condensed combustion products recovered from the filter were observed by SEM investigations coupled with energy dispersive radiation microanalysis. An illustration is shown in Fig. 2. Several structures of interest were identified in this image.

The spherical formations, labelled as 1 and 2, have an approximate diameter of $4 \mu m$. They seem to be a hollow shell of alumina. The inner part was probably aluminum, which burned mainly in the gas phase, as evidenced by the presence of nanometric alumina particles. At the end of the process, the temperature drops below the melting point of the solidifying oxide ($T_{fus_Al_2O_3} = 2345 \text{ K}$). Aluminum could still be in a liquid state, given its significantly lower melting temperature ($T_{fus_Al} = 994 \text{ K}$). The reaction with water vapor took therefore place in form of a heterogeneous surface reaction. This hollow shell structure is reminis-

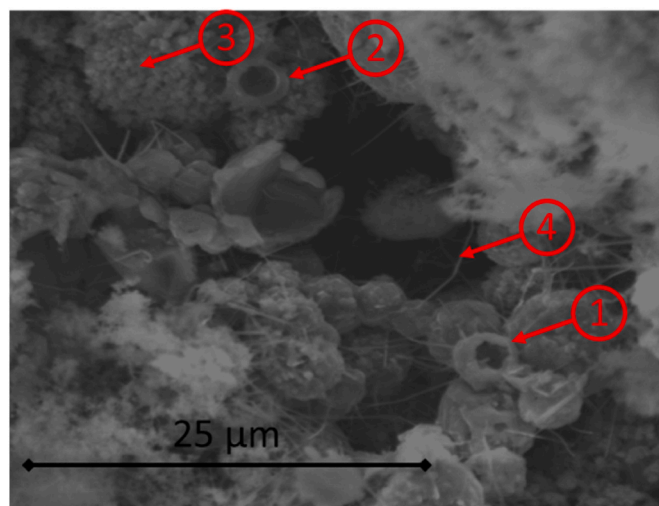


Fig. 2. Example of a SEM image of the condensed combustion products.

cent of that observed in the combustion of isolated particles in steam (see Figs. 1–21 in Ref. [10]).

Structure 3 represents a cluster of nanoparticles, each a few hundred nanometers in diameter, containing aluminum, oxygen and carbon. X-ray diffraction analysis of these samples has uncovered the presence of aluminum carbide (Al_4C_3). Filament structure 4 is very distinctive and appears to correspond to boehmite ($AlO(OH)$) filaments. The diffraction analysis also verifies the presence of minor quantities of aluminum hydrides. A key observation pertains to the crystalline structures of the discovered alumina, which are, in descending order of significance: Rhombohedral, orthorhombic and monoclinic, respectively.

3. Conclusions

This research paves the way for new possibilities to release energy. It demonstrates the co-production of heat and hydrogen with an optimal conversion rate. This scientific evidence serves as the initial stepping stone for a circular economy that relies on a process which stores energy in metals and discharges both energy (heat) as well as hydrogen based on time and location requirements. The minerals produced will be critical to the implementation of a circular economy based on this technology. Additionally, this study reveals the morphology and crystalline structures of the oxidized products. The heat released could be perfectly used in industries requiring high temperatures, such as metallurgy, the glass industry and the chemical industry. To recover the hydrogen, it will be necessary to use a cyclone and a submicron filter (of the HEPA type, for example) to recover all the solid products formed. The hydrogen can then be separated from the rest of the gas mixture by pressure swing adsorption. This method is widely used in steelworks to extract hydrogen from coke oven and conversion gases or oxygen (O_2) and nitrogen (N_2) from air. This process achieves a purity of around 99.9%. If purity is required, a membrane filter will have to be added.

CRediT authorship contribution statement

F. Halter: Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization. **D. Keo:** Investigation. **B. Grosselin:** Investigation, Formal analysis. **E. Schweers:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **L. Portugues:** Writing – review & editing, Methodology. **N. Windhab:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **U.S. Schubert:** Writing – review & editing, Supervision, Conceptualization. **C. Chauveau:** Writing – review

& editing, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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