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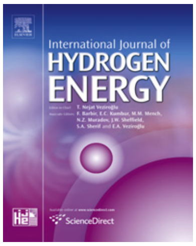

Reactivity of H_2/air mixtures over hot metal surfaces

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ABSTRACT

This paper reports on a systematic study of hydrogen oxidation in the presence of different materials, ranging from quartz to carbon steel. The reactivity tests conducted at low hydrogen concentration revealed significant promotion of the oxidation reaction by carbon steel in a temperature range (300–400 °C) where gas phase reactions occur to a limited extent. This effect is strongly enhanced by surface modifications induced by acid corrosion. Stainless steel surfaces behaved quite differently under similar reaction conditions, showing rather an inhibiting role in H_2 oxidation.

The physicochemical characterization of carbon steel samples before and after acid treatment revealed that the surface area undergoes a strong increase due to corrosion, and also the structure is modified with surface enrichment of trace metal components, which can exert a catalytic role.

The potential risk represented by the oxidation properties of these widely used materials is mitigated by the low value of the heat of combustion of hydrogen per unit volume; with a composition below the lower flammability limit, weak thermal effects were in fact observed by infrared measurements of the surface temperature. However, using a simplified kinetic expression, it can be estimated that when hydrogen-rich mixtures come into contact with an overheated metal surface, the exothermic reaction can generate dangerous hot spots.

1. Introduction

The effects of hydrogen on the structural properties of metallic materials have long been known in many fields of the manufacturing industry. An authoritative Technical Report issued by ISO in 2004 devoted a special section to detailed guidelines aimed at preventing risks associated with such hydrogen effects on different types of metals and alloys [1].

Recent research activity conducted in the perspective of hydrogen energy applications has further advanced the knowledge on the subject [2,3]. Major technological sectors, such as the gas [4], automotive [5,6] and aeropace [7] industries, have contributed significantly to this progress. As a result, embrittlement and other microstructural modifications induced in different materials by hydrogen exposure are now well recognized and their potential hazards can be securely managed in the development of hydrogen technologies.

Much less attention, though, has been devoted so far to the chemical aspects of the interaction between H_2 and metallic materials, apart from those species which are known for their catalytic properties, such as Pt, Cu, Ni.

The aforementioned ISO Report cautions to consider the role of the vessel materials on the ignition properties of hydrogen, but the issue is addressed only in general terms.

The Group at University of Calgary has devoted some studies to the high temperature effect of steel walls on the flammability properties of hydrogen. It was observed that the catalytic effect of the steel vessel could alter the flammable range of various hydrogen containing mixtures [8,9].

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However, the specific role of different materials as well as the relationship between the nature of the solid surface and its effect on hydrogen oxidation are still poorly understood.

These issues should receive due attention for their implications in many aspects of H_2 technologies, from the development of novel combustors [10,11] to the formulation of safety codes and standards.

This communication reports on a systematic study of hydrogen oxidation in the presence of different materials, ranging from quartz to carbon and alloyed steels. In parallel, extensive physicochemical characterization of the metals was carried out by surface analysis techniques.

2. Materials and methods

Hydrogen oxidation measurements were carried out in a microreactor system equipped with a fast on-line analysis apparatus. The reactor, obtained from a synthetic sapphire crystal, was 145 mm long and had an i.d. of 8 mm.

Sapphire was chosen as a suitable material for the tubular reactor not only for its chemical inertness, but also for the mechanical and optical characteristics which make it ideal for use at high temperature and for measurements with infrared techniques.

The reactor was mounted vertically inside a steel oven equipped with sapphire windows to allow measurements of internal surface temperatures with a FLIR Thermovision SC 4000 infrared imaging apparatus.

Reactants and products were analyzed on-line with a Varian CP-4900 micro gas chromatograph equipped with advanced TCD detectors and two capillary columns: Molecular sieves 5A for H_2, N_2, O_2 and Poraplot U for water. The system provides capability of analyzing permanent gases and volatile compounds in a matter of 60–90 s, with relatively high sensitivity (the detection limit was below 100 ppm in our conditions).

The reactivity of H_2 in the presence of different materials was determined in a wide temperature range, with concentrations under the lower limit of flammability, in order to avoid unnecessary constraints dictated by safety issues. Other reasons for using very lean hydrogen–air mixtures were the intention of keeping the oxidation reaction under kinetic control in order to guarantee a better repeatability of the tests with different materials, and also the consideration that an approach to the flammability range from the lean side is a realistic scenario of accidental leakage in hydrogen systems.

Typically, a mixture of air and hydrogen (2–3% v/v) was passed through the tubular reactor containing the test material at flow rates corresponding to residence times of 4–22 s. Pressure was atmospheric in all measurements.

The materials investigated are reported in Table 1.

3. Results

3.1. *Reactivity of H_2–air mixtures*

Initially the reactivity of hydrogen was determined by feeding a 2.6% H_2–air mixture to the empty reactor, which was heated from ambient temperature to 420 °C. The residence time in this test was 22 s. It can be seen from Fig. 1 that H_2 starts to react with oxygen to some extent above 200 °C; at 400 °C conversion is 11.4%. Taking into account the nature of the reactor and the low probability of contact between the gas and the tube wall, this not negligible conversion can be largely attributed to homogenous reactions; however a contribution from the reactor wall cannot be excluded. Thus sapphire turns out to be not completely inactive in these tests, and the term “reference material” seems more appropriate than “inert”.

In a subsequent set of measurements, the lower half of the reactor was filled with quartz particles and the same mixture was passed through the reactor.

Fig. 2 shows that an increase in H_2 conversion occurs compared to the empty reactor (17.6% at 400 °C against 11.4% without quartz).

These results show the effect of the contact of the gaseous reactants with quartz particles, which turn out to exert some promotion effect on hydrogen oxidation. The lower curve, corresponding to a flow rate of 100 ml/min, shows the effect of a five-fold reduction of the residence time.

The role of different metals in the H_2–O_2 reaction was evaluated by inserting into the reactor, filled with quartz particles in the lower half, different metal specimens in the form of thin plate, gauze or foil covering the internal wall of the reactor.

To check the reaction system, a material with proven catalytic properties was placed on top of the quartz bed. The Pt mesh (31 × 35 mm) gave total conversion already at 140 °C and at the higher flow rate of 100 ml/min (Fig. 3). It is interesting to note that a significant activation of the catalyst takes place under reaction conditions; in fact, the repeated test in the same conditions (curve Pt bis) revealed quite higher conversion below 120 °C. This phenomenon has been reported in studies on alkane oxidation over noble metal gauzes.

Table 1 – Materials tested for hydrogen reactivity.

Material	Composition or specification	Dimensions	Role
Sapphire	Al_2O_3	Length 145 mm i.d. 8 mm	Tubular reactor
Quartz	SiO_2 Merck pro analysis	Particles 0.2–0.8 mm	Reactor filling
Platinum	99.9% Pt	Mesh 31 × 25 mm	Reference catalyst
Stainless steel	AISI 304	Foil 30 × 5 mm; 0.06 mm thick	Reactive surface
Stainless steel	AISI 304	Mesh 29 × 40 mm; 1.13 g	Reactive surface
Carbon steel	C 0.12%; Mn 0.6%	Foil 145 × 27 mm; 0.07 mm thick	Reactive surface