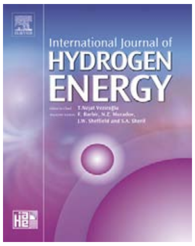
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 33 (2008) 929–936

Available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/ijhydene



Hydrogen production in the γ-radiolysis of aqueous sulfuric acid solutions containing Al_2O_3, SiO_2, TiO_2 or ZrO_2 fine particles

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ARTICLE INFO

Article history:
Received 17 November 2006
Received in revised form
2 October 2007
Accepted 30 November 2007
Available online 11 January 2008

Keywords:
Hydrogen production
Radiation chemistry
Radiolysis
Oxides
Aqueous solution

ABSTRACT

Hydrogen production was studied in the ^{60}Co γ-radiolysis of aqueous H_2SO_4 solutions containing oxide powder of Al_2O_3, SiO_2, TiO_2 or ZrO_2. The observed yields of final product H_2 increased with relative amounts of oxide powder in the solutions and exhibited a particular H_2SO_4 concentration dependence, which was different for each oxide species and its amount. The addition of a small amount of CH_3OH to a 0.4 M H_2SO_4 aqueous solution with oxide powder was quite effective for increasing the final product yields of H_2. The obtained results revealed that heterogeneous systems composed of oxide powder and aqueous H_2SO_4 solution were more efficient for producing H_2 molecules in γ-radiolysis than homogeneous systems without oxides.

1. Introduction

Hydrogen energy is very attractive as an alternative energy source in terms of easy storage and transport. Regarding global warming due to the greenhouse effect, if hydrogen production without CO_2 emission is achieved, it would be invaluable even if its running costs are somewhat higher than those for natural gas pyrolysis that emits CO_2 gas [1,2]. Many efforts have been made in the field of nuclear energy to apply nuclear heat for producing hydrogen by thermochemical processes without CO_2 emission [3–5]. Most of these production processes employ sulfuric acid decomposition at high temperature that inevitably induces corrosive conditions, which demand corrosion-resistive components for the reaction vessels [4].

In radiation chemistry, however, the γ-radiolysis of water as well as of aqueous solutions can produce hydrogen at room temperature without CO_2 emission. The reaction mechanisms to form the product H_2 have been well understood, and the yields of hydrogen formed and the kinetics of its precursors have been studied in detail [6–10]. Nevertheless, the pursuit of suitable solutions that effectively produce hydrogen is useful for achieving a lower cost hydrogen production system which causes neither CO_2 emission nor deterioration of component.

For this purpose we have been interested in heterogeneous systems consisting of a mixture of solid and aqueous solutions with an expectation that chemical reactions including hydrogen formation may be enhanced due to the presence of solids. When solids exist in solutions, exited electrons

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doi:10.1016/j.ijhydene.2007.11.028

produced from the solids under γ-irradiation are added to those from the solutions. Although the mechanism of hydrogen formation from heterogeneous systems has not been clearly understood, the enhancement in the yield of hydrogen may be ascribed, at least qualitatively, to the enhancement of excited electron yields. It is known that electrons, which act as a reducing agent, contribute to the formation of H_2 gas [6–9]. In fact there have been reports of the enhanced H_2 formation as well as of reduction of ions due to the coexistence of solids and water [11–17].

In this experiment, we investigate the effect of aqueous H_2SO_4 solutions admixed with solids in ^{60}Co γ-radiolysis on hydrogen production. This is done in order to find the experimental conditions for enhanced hydrogen yields from the viewpoint of a future use of high-level radioactive wastes (HLWs) for efficient hydrogen production. It is noteworthy that ^{137}Cs, which is the dominant γ-source of HLWs, can be used as a γ-source for this experiment, and its use promotes a new aspect of HLWs applications for hydrogen production.

2. Experiment

2.1. Materials

Each of the oxides—α-Al_2O_3, TiO_2 (anatase), ZrO_2, SiO_2 (quartz) and $SiO_2 \cdot nH_2O$ (silica gel)—was used as a material to be added to an aqueous H_2SO_4 solution to obtain a heterogeneous system. All oxides were purchased as powder, and their specific surface areas and average powder sizes are listed in Table 1.

These materials were selected not only for being corrosion-resistive in sulfuric acid solution but also for their stability under γ-irradiation. Since their energy band gaps (E_g) were as wide as 7.0–9.9 eV for Al_2O_3, 2.9–3.75 eV for TiO_2, 4.9 eV for ZrO_2 and 8.0–11.0 eV for SiO_2 [18], the photolysis of water containing most of these oxides was unlikely to produce hydrogen gas. This is because electrons are hardly excited from a valence band to a conduction band by visible or near UV light radiation in these oxides [19]. On the other hand, we can expect that γ-radiation can produce excited electrons associated with enhanced hydrogen formation. In addition, the high penetration capability of γ-radiation can increase the reaction volume as compared to photolysis in any experimental conditions, which would result in increasing the total volume of hydrogen gas produced.

2.2. Sample preparation

Samples for γ-irradiation were composed of aqueous H_2SO_4 solution, oxide and air space: a certain amount of oxide powder was added to a 2 ml aqueous H_2SO_4 solution in a vial of about 5 ml, and the mouth of the vial was sealed by screwing a cap with a septum of PTFE/silicone. The air space of the vial (about 3 ml in volume) was not in general converted into N_2 gas prior to γ-irradiation, but was bubbled with N_2 gas for deaeration when CH_3OH was added to dilute H_2SO_4 solutions or 100% CH_3OH solutions.

The maximum amount of oxide added in a 2 ml solution depended on the bulk density of the oxide powder in 0.4 M H_2SO_4 solution as listed in Table 1: for instance, 70 wt% was possible in the case of ZrO_2 powder, 50 wt% for α-Al_2O_3 powder, 50 wt% for $SiO_2 \cdot nH_2O$ powder and 33 wt% for TiO_2 powder.

Water purified by distillation and deionization, whose electric conductance was nominally $<0.05\,\mu S$, was used for water radiolysis experiment as well as for dilution of 98 wt% H_2SO_4 solution to obtain a certain aqueous H_2SO_4 concentration. The prepared concentration ranged from 0.2 to 4 M prior to addition of oxide powder. The measured pH of the purified water, which was exposed to air, was 5.8 prior to γ-radiolysis due to absorption of CO_2 in air and shifted to 6.9 after γ-radiolysis probably because of reduction induced by hydrated electrons (e^-_{aq}) originated from γ-irradiation [6].

2.3. γ-ray irradiation

Irradiation of γ-rays at ambient temperature for low dose experiments (<10 kGy) was performed using a ^{60}Co γ-source at JAEA-Tokai with a dose rate of about 1 kGy/h, while for high dose experiments (>10 kGy) a ^{60}Co γ-source at JAEA-Takasaki with a dose rate of 10–30 kGy/h was used. Here, the value of 1 kGy is equivalent to the energy of 1 kJ absorbed in a mass of 1 kg.

Our experiments were mainly intended to show the qualitative tendencies of heterogeneous effects in a fairly wide range of combinations of oxides and aqueous sulfuric

Table 1 – Specific surface areas, average powder sizes and bulk density of oxides in 0.4 M H_2SO_4 aqueous solution

	α-Al_2O_3 [a]	TiO_2 [b]	ZrO_2 [c]	SiO_2 [d]	$SiO_2 \cdot nH_2O$ [e]
Specific surface area (m^2/g)	15	239	3	15	645
Average powder size (μm)	0.2	0.02	50	0.8	215
Bulk density (g/ml)	0.8	0.6	2.5	–	0.7

[a] 99.99 wt% purity α-Al_2O_3 named AKP-50 (Sumitomo Chemical Co., Japan).
[b] 90 wt% purity anatase TiO_2 named PC101 (Titankogyo Co., Japan).
[c] 99.99 wt% purity ZrO_2 (Furuuchi Chemical Corp., Japan).
[d] Quartz type 99.9 wt% SiO_2 (Kojundo Chemical Lab Co., Japan).
[e] Gel type $SiO_2 \cdot nH_2O$ (GL Sciences Inc., Japan).