

Catalytic Water Decomposition via Novel Bimetallic Systems

K. M. JEONG

Avco Research Laboratory, Inc., 2385 Revere Beach Parkway, Everett, Massachusetts 02149

AND

H. E. SWIFT¹

University of Pittsburgh, Foundation for Applied Science and Technology, University Technology Development Center Two, 3400 Forbes Avenue, Pittsburgh, Pennsylvania 15213

Received October 18, 1985; revised April 10, 1986

The production of hydrogen via the catalyst-assisted decomposition of water was investigated under mild conditions for the reaction $\text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2$. Hydrogen yields were determined for reaction temperatures of 303, 333, and 353 K at various time intervals. The extent of reaction completion varied from a few percent to about 95%. The catalyst systems investigated consisted of the following metals electrochemically dispersed on the Zn surface: Ag, Ni, Fe, Au, Pd, Ru, and Rh. Except for Ag and Ni, addition of the other metals to zinc enhanced the production of hydrogen. The order of promoting effect was found to be $\text{Rh} > \text{Pt} > \text{Ru} > \text{Pd} > \text{Au} > \text{Fe} > \text{no catalyst} > \text{Ni} > \text{Ag}$. Kinetic data obtained closely fit a homogeneous sphere topochemical reaction model. © 1986 Academic Press, Inc.

INTRODUCTION

Emerging energy considerations during the last decade have resulted in the reassessment of many manufacturing technologies and in the reallocation of natural resources. Although several commercial processes are available for the manufacture of hydrogen, catalytic steam reforming of light hydrocarbons remains the preferred method, primarily due to low overall costs and high quality of product (1). Due to projected declining supplies of natural gas and naphtha, the commercial production of hydrogen, which as traditionally relied on these source feedstocks, is of current interest.

Numerous alternate primary energy sources have been proposed, particularly in response to the development of synthetic fuels liquefaction and gasification industries and the refining/upgrading of heavier petroleum crudes and synfuels. Concurrently,

new methods of producing hydrogen are being evaluated which have prompted renewed interest in the fundamental process of water splitting. The principal objective of this work was to investigate the production of hydrogen by such a method based on the catalytic decomposition of water under mild conditions.

Interest in closed-loop thermochemical cycles requiring only water is primarily ascribed to their potentially higher thermal efficiencies compared to water electrolysis. The energetics and thermodynamics of several closed-loop processes have been reported; for example, those based on vanadium-chlorine (2) and sulfur dioxide-iodine. (3) Bamberger and Richardson (4) have compiled a listing of 72 such systems. The majority of these are conceptual in nature, mainly based on estimated thermodynamic properties.

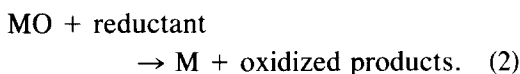
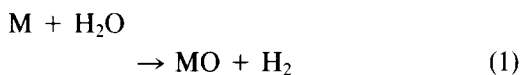
In contrast, open-loop cycles for water splitting are based on favorable thermodynamics due to the addition of another reactant, usually an active metal. The result is a

¹ To whom all correspondence should be addressed.

set of reduction–oxidation reactions with negative free energy charges at standard conditions. The simplest cycle is the so-called water–gas shift reaction, i.e., $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, where the oxidation of CO to CO_2 offsets the thermodynamically unfavored decomposition of water at standard conditions.

An example of a commercial open-loop cycle is the steam iron process (5). General Electric has investigated a similar process based on tin (6). Few systems, however, have been identified which proceed at enhanced rates due to catalysts. An extensive study of various metal/metal oxide redox systems was carried out by Morikawa and co-workers (7, 8), principally using carbon as the reductant. In subsequent studies (9–11) these researchers examined the effects of different metal oxides, additives, and carriers for hydrogen generation at temperatures ranging from 473 to 973 K. Examples of materials reported to have catalytic properties were CuO, Pd, and Pt (9). McGuiggan *et al.* (12) reported a process for the production of hydrogen from hydrogen sulfide decomposition using metal boride, nitride, carbide, and silicide catalysts.

The generation of hydrogen from water decomposition has been limited by the slow rates of the redox steps, suggesting the addition of catalytic materials to enhance the reaction under mild conditions. This involves the reduction of water by an active metal to yield hydrogen and the reduction of the corresponding metal oxide to regenerate the metal, i.e.,



In this paper, results are presented for the Zn/ZnO reaction system (1) at temperatures of 303, 333, 353 K in the presence of the following metals: Ag, Ni, Fe, Au, Pd, Pt, Ru and Rh. The catalytic systems consist of

one of these metals electrochemically deposited on the Zn surface.

EXPERIMENTAL

The compositions of the Zn/catalytic metal systems were: 0.68 mole% Au, Pd, Pt, Ru and Rh; 0.82 mole% Ni; 0.98 mole% Ag; and 1.14 mole% Fe. The rate of hydrogen production was found to be only slightly dependent on the catalytic metal concentration for the mole fractions used in this work. The Zn/metal systems were prepared by dissolving one of the following salts in 100 ml of ultrapure distilled water: $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$; $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$; $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$; $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$; PdCl_2 ; AgNO_3 ; PtCl_4 ; and $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$. The slightly acidic aqueous solutions were neutralized with aqueous KOH. Blank experiments showed no catalytic effects due to neutralization by KOH. Zinc powder (about 100 mesh) was then added and the mixture stirred for 5 min. The black powder, formed by the electrochemically deposited metal on Zn, was filtered, washed with copious quantities of ultrapure distilled water (air oxidation minimized), and then dried in vacuum with nitrogen purging at 333 K. The resulting filtrates were colorless in almost all cases, indicating complete desorption of the metal ions on zinc.

The surface properties of the Zn/metal complexes were analyzed using the BET method with nitrogen adsorption at 77 K, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Hydrogen production yields were measured at various times by adding 3 g of the Zn/metal materials to 225 ml of nitrogen-purged distilled water contained in a three-neck flask. One port had a nitrogen purge; the other was used to add the solids, and the third attached to a gas buret for collection hydrogen by water displacement. After addition of solid, the nitrogen purge was stopped and the port sealed with a rubber septum cap. Since hydrogen was collected by water displacement, the yields were corrected to standard cubic centimeters. Zn

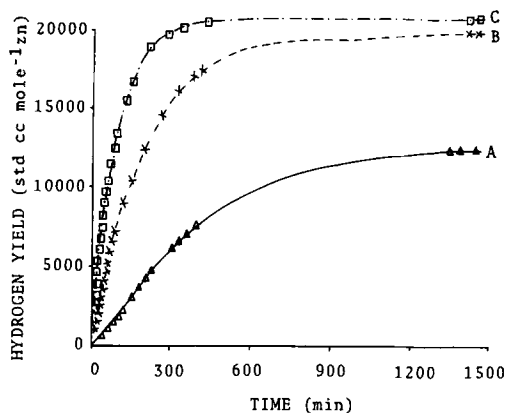


FIG. 1. Effect of temperature for the Rh-catalyzed reaction of $\text{Zn} + \text{H}_2\text{O}$: (A) 306 K, (B) 333 K, (C) 353 K.

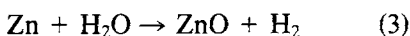
powder and Rh powder (both 100 mesh) were also evaluated.

RESULTS AND DISCUSSION

The reaction of excess Zn with aqueous solutions metal salts such as RhCl_3 was rapid and complete. SEM and XPS results revealed that a uniform coating of zero valent metal is deposited on Zn. In the case of Rh, the reaction is



The reaction is not balanced, since excess Zn was used. The resultant material was immediately filtered, washed, and dried in vacuum. Addition of this material to water at room temperature generated hydrogen due to the reaction



with the formation of ZnO as verified by XPS. The intimate contact of certain metals such as Rh with Zn was necessary for this reaction to occur at mild conditions. Zn or Rh powder alone did not decompose water at these conditions.

The rates of hydrogen production were determined at 303, 333, and 353 K for Zn bimetallics of Pd, Pt, Ru, and Rh and at 353 K for Zn bimetallics of Ag, Ni, Fe, and Au. With the exception of Ag and Ni, the addition of the second metal promoted water

decomposition without passivation of the Zn surface. For the metals Pd, Pt, Ru, and Rh, a positive temperature dependence was observed. These qualitative features of the experimental data, displayed a plots of hydrogen yield versus time, were examined by a kinetic analysis in order to compare catalytic effects and suggest a mechanism for the decomposition of water.

Hydrogen yield curves from the Zn/Rh system are shown in Fig. 1. These data show a rapid increase in hydrogen yield at early reaction times. In contrast, the Zn/Fe and Zn/Au systems proceeded at much slower rates, giving a smaller percentage of reaction completion. First order fits at 353 K

$$\ln(1 - f) = -k^t t + c \quad (4)$$

of these data are shown in Fig. 2. The ordinate axis represents the degree of oxidation of Zn and is evaluated from the fraction of hydrogen produced at time t , denoted by f . The rate of hydrogen generation was calculated by multiplying the first-order rate constant k^t by the final amount of hydrogen recovered. As indicated in Fig. 2, a good agreement is obtained between the experimental data and calculated values. These results will be discussed later and compari-

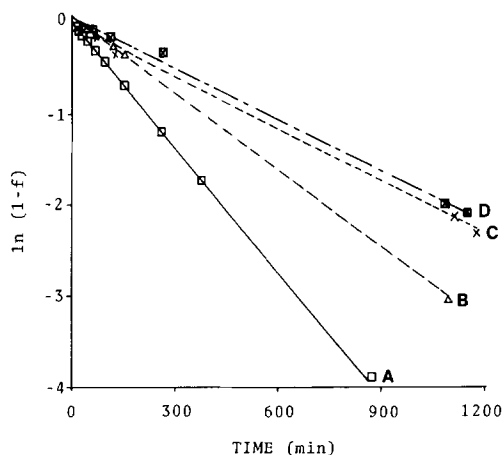


FIG. 2. First-order plots of H_2 yield for the $\text{Zn} + \text{H}_2\text{O}$ reaction at 353 K catalyzed by various metals: (A) Zn/Rh, (B) Zn/Pt, (C) Zn/Ru, (D) Zn/Pd.

TABLE 1
Comparison of Hydrogen Production Rates and Activation Energies
for Step 1

Catalyst	$T = 303 \text{ K}$		$T = 333 \text{ K}$		$T = 353 \text{ K}$		E_a^c
	k^{1a}	Rate ^b	k^{1a}	Rate ^b	k^{1a}	Rate ^b	
Ag	—	—	—	—	0.0073	0.0083	—
Ni	—	—	—	—	0.017	0.0040	—
Zn alone	0.0026	0.00062	0.091	0.015	0.41	0.13	23
Fe	—	—	—	—	0.59	0.69	—
Au	—	—	—	—	0.63	5.0	—
Pd	0.61	0.28	3.2	8.5	9.5	37	12
Ru	1.4	3.8	3.3	14	12	53	9
Pt	2.4	2.5	4.6	19	15	62	8
Rh	3.5	8.8	7.9	34	20	84	8

^a k^1 in units of 10^{-5} s^{-1} .

^b Rate in units of $10^{-7} \text{ mole s}^{-1}$.

^c E_a in units of kcal mole^{-1} .

sons made with topochemical reaction models.

For the Zn/Pd, Ru, Pt, and Rh bimetallics and the Zn only system, apparent activation energies E_a were determined from fits of the bimolecular rate constants k to the Arrhenius expression

$$k = A e^{-E_a/RT}. \quad (5)$$

The accuracy of the calculated E_a values, $\pm 2 \text{ kcal/mole}$, reflects the limited temperature range covered and the uncertainties in the bimolecular rate constants. The latter are primarily due to ambient temperature and pressure fluctuations amounting to about 5%. The results of the kinetic analysis are summarized in Table 1, which lists the first-order rate constants, rates of hydrogen generation, and activation energies.

The rate of hydrogen productions using only Zn powder was determined as reference points. At room temperature, the reaction of Zn with water to yield hydrogen has an enthalpy of $H = -15 \text{ kcal/mole}^{-1}$ and a free energy change of $\Delta G = -19 \text{ kcal/mole}^{-1}$. Based on thermodynamic considerations, the reaction is highly favorable and becomes more exothermic at higher tem-

peratures. While these data indicate an increase in hydrogen generation with temperature, the rates are slow: 6.2×10^{-11} , 1.5×10^{-9} , and $1.3 \times 10^{-8} \text{ mole s}^{-1}$ at 306, 333, and 353 K, respectively. At 353 K, the reaction was only 7% complete after 22.3 h. The two hundred-fold enhancement from 306 to 353 K reflects a positive temperature dependence in the overall reaction mechanism, which is expected to extend to higher temperatures until the melting point of Zn is reached and aggregation effects become important. The activation energy was determined to be about $23 \text{ kcal mole}^{-1}$ and is comparable to values determined by Morikawa and co-workers (9, 11) for the Sn/SnO₂ and In/In₂O₃ systems.

In sharp contrast to the Zn results, significant catalytic effects were observed for the addition of Pd, Ru, Pt, or Rh to Zn, resulting in hydrogen production rate values ranging from 2.8×10^{-8} to $8.4 \times 10^{-6} \text{ mole/s}$. These data represent factors of approximately 3×10^2 to 1.4×10^4 enhancements in hydrogen yields. Of particular significance is the large increase in room temperature rates for these systems. Following a reaction time of 24 h at 303 K, the water decomposition process was observed to

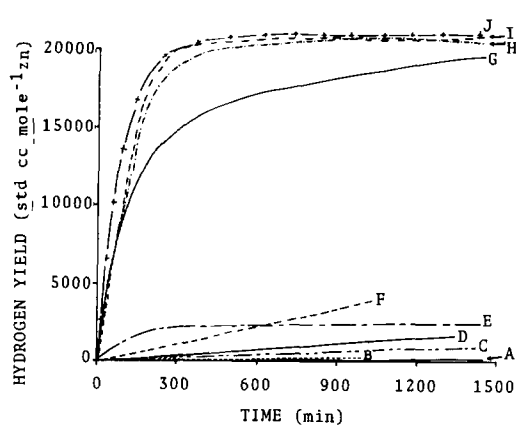


FIG. 3. Effect of various metals on reaction of Zn + H₂O at 353 K: (A) Zn/Ag, 0.98 mole%; (B) Rh; (C) Zn/Ni, 0.82 mole%; (D) Zn; (E) Zn/Fe, 1.14 mole%; (F) Zn/Au, 0.68 mole%; (G) Zn/Pd, 0.68 mole%; (H) Zn/Pt, 0.68 mole; (I) Zn/Ru, 0.68 mole%; (J) Zn/Rh, 0.68 mole%.

proceed to 10, 23, 38, and 56% of completion for bimetallic systems employing Pd, Pt, Ru, and Rh, respectively.

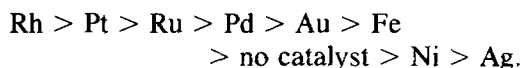
As indicated by the data in Table 1, enhanced catalytic effects were also determined for reactions at 333 and 353 K. The most favorable promoting effect was for the Zn/Rh system. At 353 K after 24 h, the reaction was 93% complete. The larger hydrogen yields determined for the Pd, Ru, Pt, and Rh systems correspond to decreases in the activation barrier from 23 kcal/mole to values near 10 kcal/mole.

Based on these significant enhancements in hydrogen generation, blank experiments were performed in order to further understand the reaction mechanism. Pure Rh powder was contacted with water in the absence of Zn at 353 K. No evolution of hydrogen was detected. The promoting effect of the Rh catalysts is thus ascribed to interactions at the boundary between Rh and Zn, rather than to additional chemical reactions involving Rh alone.

Measurements of hydrogen yields were made at 353 K for Zn bimetallics of Fe, Au, Ag, and Ni (see Table 1). Only minor enhancements in hydrogen production were

found for the Fe and Au bimetallics. The hydrogen rate compared to Zn roughly doubled for Fe and increased by about a factor of four for Au. Bimetallics of Ag and Ni retarded water decomposition compared to using only Zn. Thus, the chemical properties of the solid-liquid interface associated with the dispersed metal on Zn can enhance or retard the water splitting process.

The effects of the eight Zn/metal systems on hydrogen generation at 353 K are shown in Fig. 3. The first-order rate constants and activation energies in Table 1 parallel the qualitative features shown by these plots. The order of promoting effect of these metals is



There are no previously reported data to use for comparison for water decomposition. In a related study, Otsuka *et al.* (8) determined that the reduction of ZnO by carbon at 973 K, followed by oxidation of Zn at temperatures between 673 and 773 K, yielded no hydrogen. These results are consistent with the very slow hydrogen production rates listed in Table 1 for Zn. In order to take advantage of the enhanced hydrogen yields determined for Zn/ZnO with the metals Pd, Ru, Pt, and Rh as well as the regeneration of the primary metal by a two-step oxidation-reduction cycle, the results of Otsuka *et al.* (8) indicate that the most effective systems are those for which both steps of the cycle have free energy changes near zero.

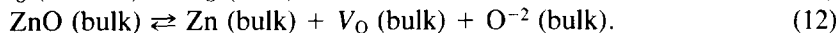
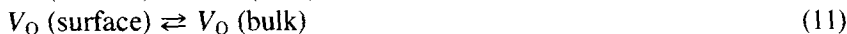
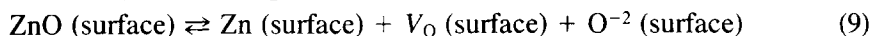
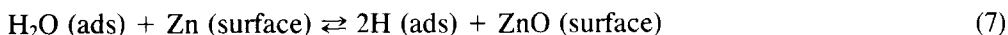
The catalyst-assisted decomposition of water by a metal such as Zn is described as a topochemical reaction in that the reaction is localized at the interface between the solid substrate and the solid product. The experimentally measured hydrogen production rates are a function of the rate of chemical reaction and the surface area of the reaction interface. The former process is a function of species concentration and temperature, while the latter effect is time dependent. These factors have been incorpo-

rated in the following topochemical reaction models: formation and growth of nuclei, shrinking sphere, and homogeneous sphere. Since the detailed assumptions of each model are different, the derived mechanistic expressions yield different functional dependences.

As previously described, good fits of the observed kinetic curves were obtained for Eq. (4), which also holds for the homogeneous model. These data could not be fit to expressions obtained for the formation and growth of nuclei or shrinking sphere

models. This suggests that the homogeneous sphere model is the probable reaction model for the catalyzed Zn to ZnO reaction. According to this model, the reaction interface remains constant and the solid product formed at the reaction interface rapidly diffuses to the bulk of the substrate grains. The result is a homogeneous distribution during reaction both at the reaction interface sites and in the bulk substrate grains.

The chemical reactions have been modeled assuming the following steps:



Equations (10) and (11) represent the diffusion of oxygen ions and oxygen ion vacancies (V_{O}) between the surface and bulk in order to assure a homogeneous distribution of the ZnO product during the course of reaction.

While the homogeneous sphere topochemical reaction model provides a general framework for the above scheme of solid-liquid and solid phase interactions, the application to the reported bimetallic systems is not straightforward. This is because metals can cause both positive and negative effects on hydrogen generation and variations in surface area values. The surface area of Zn powder is about 0.03 m²/g. After addition of the second metal and testing for hydrogen production, the surface areas varied between 0.5 and 2 m²/g. No correlation was found between activity and surface area values. For example, surface areas close to 2 m²/g were found for the Zn/Ag

and Zn/Ni materials, which yielded negative hydrogen production results. The surface areas obtained on these low area materials by nitrogen absorption have some uncertainty, and this is an area requiring more evaluation before definite conclusions can be reached concerning the role of surface area changes and reactivities for these bimetallics.

Additional kinetic data are required to more fully explain activity differences. The correlation of increasing hydrogen yield with decreasing activation energies indicates that chemical modifications strongly influence the properties at the reaction interface. This offers an area for further investigation.

ACKNOWLEDGMENTS

The authors acknowledge the Chevron Corporation for permission to publish this manuscript and Mr. J. E. Bozick for conducting many of the experiments.

REFERENCES

1. Kermode, R. I., in "Hydrogen: Its Technology and Implications" (K. E. Cox and K. D. Williamson, Jr., Eds.), p. 61. CRC Press, Cleveland, 1977.
2. Funk, J. E., and Reinstrom, R. M., Final Report-ERD 3714, Vol. II, Suppl. A, Allison Division of General Motors Corporation for USAEC, 1964.
3. "Development of Thermochemical Water Splitting for Hydrogen Production at General Atomic Company," General Atomic Report GA-A14050, September 30, 1976.
4. Bamberger, C. E., and Richardson, D. M. *Cryogenics* **6**, 197 (1976).
5. Tarman, P. B., "Developmental Hydrogen via Coal Gasification Processes," IGT Symposium on Hydrogen for Energy Distribution, July 24-28, 1978, p. 239.
6. Spacil, H. S., U.S. Patent 3,821,362, June 28, 1974.
7. Otsuka, K., Takizawa, Y., and Morikawa, A., *Fuel Process. Tech.* **6**, 215 (1982).
8. Otsuka, K., Murakoshi, S., and Morikawa, A., *Fuel Process. Tech.* **7**, 203 (1983).
9. Otsuka, K., Murakoshi, S., and Morikawa, A., *Fuel Process. Tech.* **7**, 213 (1983).
10. Otsuka, K., Hatano, M., and Morikawa, A., *J. Catal.* **79**, 493 (1983).
11. Otsuka, K., Shibuya, S., and Morikawa, A., *J. Catal.* **79**, 392 (1981).
12. McGuiggan, M. F., and Kuch, P. L., U.S. Patent 4,447,409, May 8, 1984.