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and G.A. Somorjai

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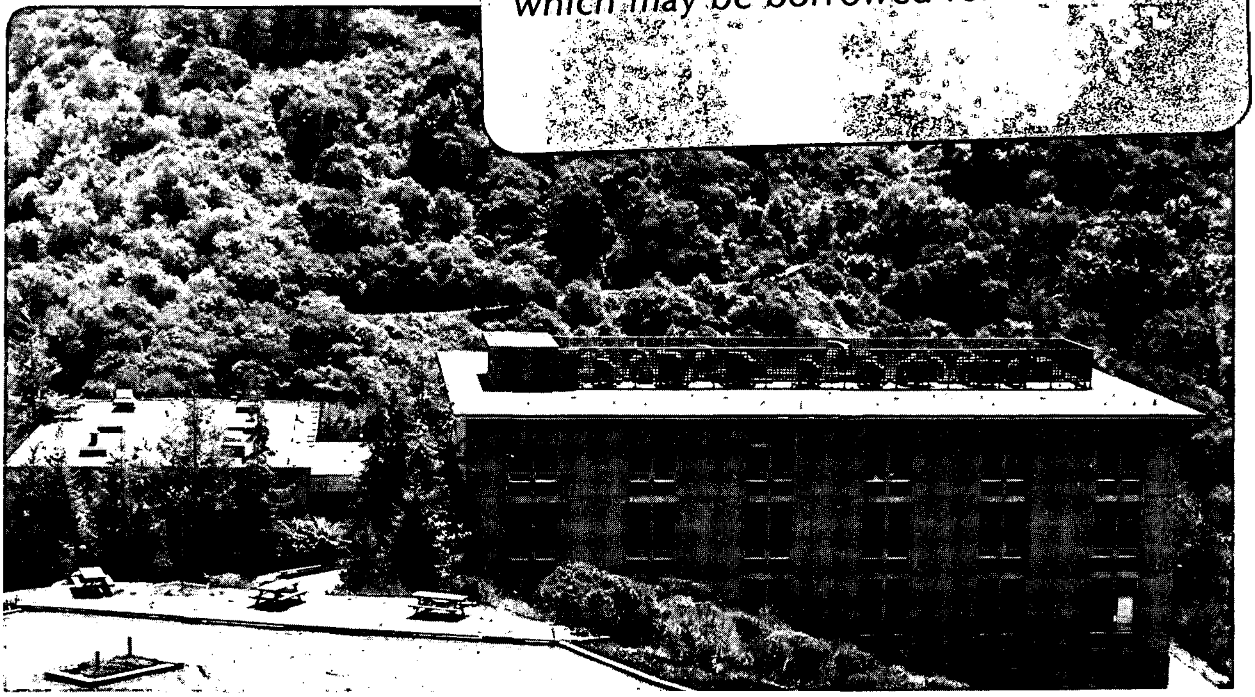

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PHOTOASSISTED CATALYTIC DISSOCIATION OF H_2O AND REDUCTION OF N_2 TO NH_3 ON PARTIALLY REDUCED Fe_2O_3

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ABSTRACT

H_2 and NH_3 were produced when suspension of Fe_2O_3 catalyst particles or sintered pellets in water were illuminated with light of energy greater than 2.3eV. Catalytic action was demonstrated by detecting H_2 yields many times the stoichiometric equivalent of the measured (by X-ray diffraction, Mossbauer spectroscopy and oxidimetry) Fe(II) content of the catalyst up to 80x for H_2 and 20x for NH_3. The initial rate of formation of H_2 was 40µmoles/hr.g catalyst and of NH_3 was 10µmoles/hr.g catalyst. The formation of O_2 was proved by mass spectrometric observation using ^{18}O labelled water.

END OF ABSTRACT

We report here the catalytic photoassisted splitting of water into H_2 and O_2 and the photoassisted reduction of N_2 with water to NH_3. The catalyst consists of a mixture of approximately 90% α-Fe_2O_3 and 10% Fe_3O_4 as determined by x-ray diffraction. Mossbauer experiments also detect the presence of Fe_3O_4 in similar amounts. Other phases of the iron oxide, like γ-Fe_2O_3 could also be present in small amounts.

α-Fe_2O_3 is an n-type semiconductor with a band gap of about 2.3eV[1]. It can absorb at least 40% of the solar flux. It has, accordingly, been investigated as a light absorbing electrode for photoassisted electrolysis of water[2-12], and as a catalyst in the photoassisted reduction of N_2 to

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ammonia by water[13] or by aqueous organic solutions[14]. The photoassisted production of H_2 from H_2O using Mg-doped Fe_2O_3[15,16] and of NH_3 from N_2 using Fe-doped TiO_2[17,18] has already been reported. Because of the poor yields, the catalytic nature of these processes could not be assessed. The iron oxide catalyst that we report here is much more active than the iron containing samples that were previously utilized. The catalytic nature of the reactions could thus be demonstrated.

We used the catalyst both in the forms of powder and as sintered pellets. It can be prepared in powder form by exposing α-Fe_2O_3 (Alfa prod. 99.9%) for 8 hours at 450°C and 1 atm to a flowing mixture of 70% H_2 and 30% H_2O vapor and then heating in O_2 or air at 450°C for 10 min. One-half inch diameter sintered pellets of iron oxide were prepared by pressing the powder to 7000 Kg/cm^2 and then heating in air for 20 hr at 1150°C. The pellets could be activated by reacting first with 70%H_2-30%H_2O at 500°C and 1 atm for 10 min. and then with O_2 or air at 450°C for 10 min.

The composition of the catalyst was estimated from its X-ray powder diffraction pattern by comparing the ratio of the integrated intensities of the (220) spinel and (012) corundum reflections with known standards of spinel and α-Fe_2O_3. This analysis indicated that the material contains more than 90% Fe_2O_3 and less than 10% Fe_3O_4. The Mossbauer spectrum also indicated that the major component is α-Fe_2O_3 (H=515 kOe, ε=0.12mm/s, IS=0.60mm/s with respect to SNP). Fe_3O_4 was detectable but constituted less than 10% of the catalyst. Oxidimetric analysis of solutions of the dissolved catalyst in aq. HCl with $KMnO_4$[19] indicated that 3-5 atom% of the iron in the catalyst is Fe(II). BET measurement showed a surface area of 1.85 m^2/g of the powdered catalyst.

To measure the hydrogen yield, the reaction was performed in a closed loop with either N_2 or Ar circulating through a suspension of 30mg of catalyst in 30ml of deionized water in a thermostated pyrex cell (Temperature 29-30 C). The suspension was illuminated with 20mW of light from a 150W Xe lamp. The gas stream was periodically leaked into a UHV chamber where it was analyzed with a calibrated quadrupole mass spectrometer. In its pure form neither α-Fe_2O_3 nor the reduced form of the oxide, Fe_3O_4, are active as photocatalysts. Assuming that all the catalyst particles were active during the experiment, the initial rate of hydrogen formation was 40 μ moles/hr.g catalyst. To determine the yield of ammonia, N_2 gas was bubbled through the aqueous slurry of catalyst and illuminated by 20mW of light. The gas stream was subsequently passed through a trap containing dilute aq. HCl at 0-4°C. Aliquots of solution from both the cell and the trap were analyzed spectrophotometrically by the trichloramine method[20] The initial rate of ammonia formation was 10 μmoles/hr.g catalyst. We can roughly express the rate in terms of catalyst surface area. For our experimental conditions the result is 100 μ moles/hr.m^2 (which would be equivalent to 0.5 μ A/cm^2), assuming that only half of the particles are illuminated on one side at any given time.

By using Ar instead of N_2 as the circulating gas, ammonia production was less than the detection limit of the trichloramine method(2×10^{-8} moles)[20] In the case of H_2, the yield was unaffected by using Ar instead of N_2 as the circulating gas. NH_3 and H_2 and O_2 thus appear to be formed in parallel processes.

The production of both H_2 and NH_3 was only observed when the catalyst was illuminated with light of wavelength shorter than 540nm. When the reaction was carried in the dark neither H_2 nor NH_3 was observed.

The formation of O_2 was demonstrated by using a pellet suspended in 3ml of water labelled with ^{18}O and detecting products of mass 36, 34 and 32 mass-spectrometrically.

The observed O_2 to H_2 ratios varied between 0.41 and 0.51 in four different measurements.

The oxidation products formed in the NH_3 reaction are not yet known at present.

The results of these experiments are presented in the figure. Our studies demonstrate that the catalyst remains active for production of both NH_3 and H_2 for about 450hr. Assuming that the catalyst contained 5 atom% of Fe(II) (in the form of Fe_3O_4), the yield of H_2 obtained in about 450hr would be equivalent to 80 times the stoichiometric reducing capacity of the catalyst while the yield of NH_3 obtained in about 580hr of illumination would be equivalent to 20 times the stoichiometric reducing capacity of the catalyst. In fact, no significant consumption of Fe(II) was detected either by X-ray diffraction or by oxidimetric measurements on samples of the used catalyst. It can be concluded that the observed reactions are catalytic. As can be seen in the figure a significant decay of catalytic activity was observed after several hundred hours of illumination. The reasons for this decay are under investigation. A more detailed account of these and other experiments will be published in a forthcoming paper.

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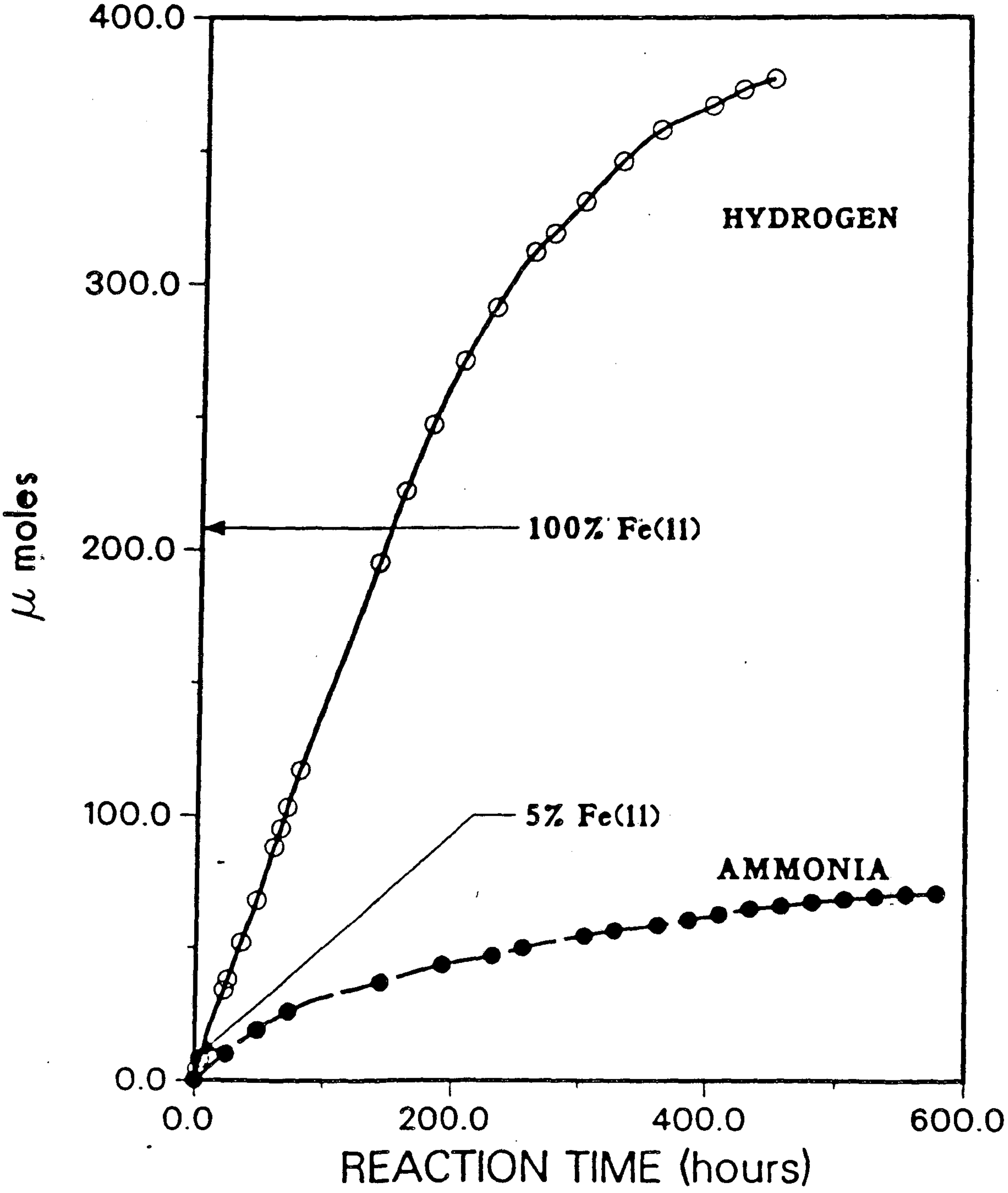
FIGURE CAPTION

Cumulative amounts of H_2 and NH_3 obtained from photodissociation of H_2O and photoreduction of N_2 by 20mW of light of energy greater than 2.3eV. The catalyst consist of aqueous suspensions of partially reduced particles of iron oxide. For comparison we indicate the amounts of H_2 that would correspond to the stoichiometric oxidation of Fe(II) by H_2O in samples containing 100% and 5% Fe(II) respectively.


400.0
300.0
200.0
100.0
0.0
μ moles
HYDROGEN
100% Fe(II)
5% Fe(II)
AMMONIA
0.0
200.0
400.0
600.0
REACTION TIME (hours)

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