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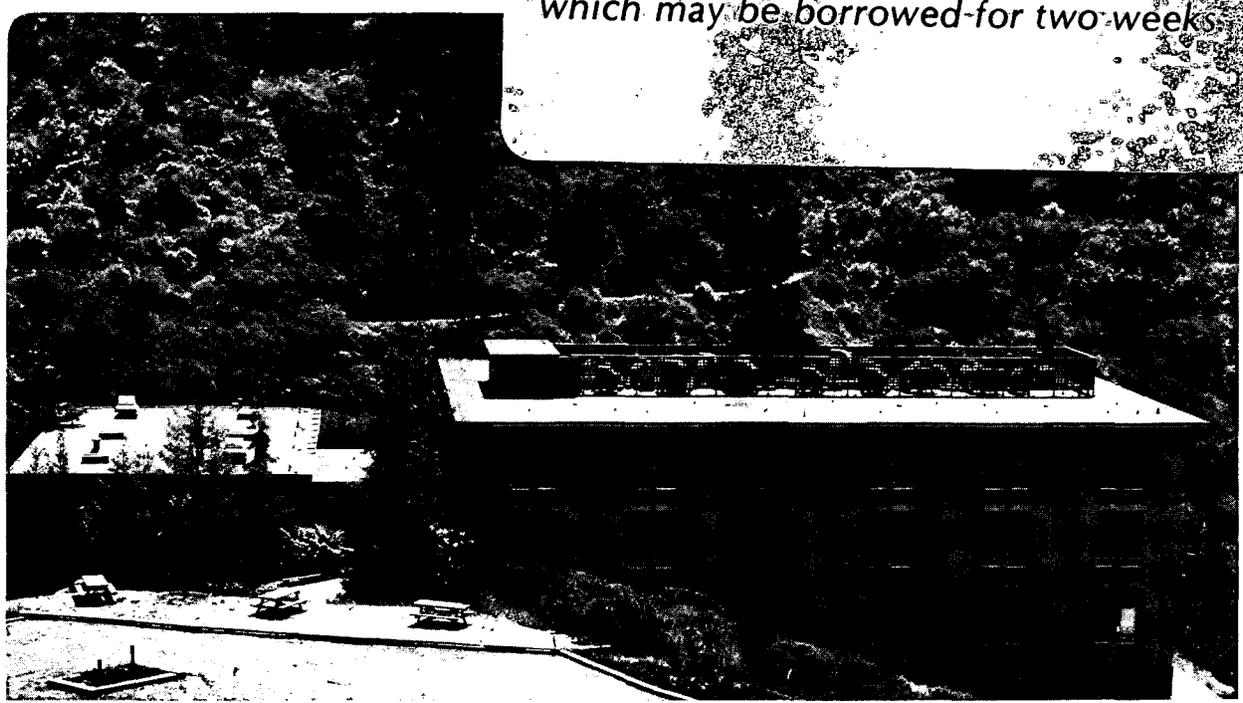
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FROM A WATER-METHANOL MIXTURE WITH
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H. Nakanishi, C. Sanchez, M. Hendewerk, and
G.A. Somorjai

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Photochemical Hydrogen Production from a Water-Methanol
Mixture with Iron Oxide Suspensions

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Abstract

Photochemical hydrogen production has been detected from small particles of doped iron oxide suspended in a methanol-water (1:1) mixture. The systems studied consisted of a pure n-type semiconductor, $\text{Fe}_{2-x}\text{Nb}_x\text{O}_3$ ($x = 0.02$), a pure p-type semiconductor, $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.25$), and Mg-doped $\alpha\text{-Fe}_2\text{O}_3$. The efficiency of the reaction increased substantially when the powders were loaded with Pt. Of the systems investigated Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ showed the highest efficiency. In the case of Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ the existence of spinel phase inclusions in the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure remarkably enhances the photocatalytic reactivity, which may be a result of a cathodic shift of the conduction band edge of the corundum structure and also an increase in the conductivity of the material. Hydrogen production from these Mg-doped iron oxides is photocatalytic and occurs mainly as a result of bandgap irradiation, but also occurs with sub-bandgap illumination. There is a linearly increasing dependence of the H_2 production with increasing light intensity.

Introduction

Since the discovery of the possibility for the photodissociation of water using semiconductor electrodes (1), there has been a renewed interest in photoelectrochemical and photocatalytic processes at semiconductor-electrolyte interfaces because of the possible application of converting solar energy into electrical or chemical energy (2). In 1977 Schrauzer et. al. (3) showed that small amounts of water could be decomposed to form H_2 and O_2 when semiconductor particles were irradiated with light. After that Bard (4), Sakata (5), and Sato (6) discovered that even higher quantum efficiencies for H_2 production could be obtained from water, water-alcohol, and other reaction systems using Pt-deposited semiconductor powders such as TiO_2/Pt or CdS/Pt . Such treatment of the semiconductor particles decreases electron hole pair recombination and also catalyzes hydrogen recombination on the surface (7). More recently, this cooperative effect between the deposited metal catalysts and the underlying semiconductors has been compared to the phenomenon of strong metal support interactions (8). There have been many discussions about suitable materials for photocatalytic reactions using solar energy (2). Iron oxide is one of the best candidates for such reactions. It is abundant and therefore inexpensive, and it is stable in both acidic and basic aqueous solutions. The most attractive feature is that it has a bandgap of 2.2 eV (9) which is in the visible region of the solar spectrum and allows the utilization of 40% of the radiation from the sun. The photoelectrochemical characteristics of n-type iron oxides for water decomposition using $\alpha-Fe_2O_3$ or metal-deposited $\alpha-Fe_2O_3$ in the form of single crystals (10), polycrystalline discs (11), and thin films (12) has been extensively studied. Recently, we reported the structural and

photoelectrical properties of a polycrystalline magnesium-doped $\alpha\text{-Fe}_2\text{O}_3$ material (13) exhibiting p-type behavior. It is important to know the photocatalytic nature of Fe_2O_3 for the application of solar energy conversion. However, almost no studies of iron oxide small particle systems for photocatalytic reactions have been reported (14)(15) in comparison to the many studies conducted using TiO_2 , SrTiO_3 , CdS , InP , or ZnO powders (4)(5)(6)(16). This is due mainly to the low efficiency exhibited by iron oxides for H_2 photogeneration reactions.

In this paper we present the results of investigations of the photocatalytic hydrogen production abilities of magnesium-doped $\alpha\text{-Fe}_2\text{O}_3$ polycrystalline powders, and in particular, the positive effect of spinel phase inclusions in the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure for catalytic H_2 production. We compare the reactivities of magnesium-doped $\alpha\text{-Fe}_2\text{O}_3$ with a pure n-type and a pure p-type semiconductor based on iron oxide. We prepared Nb-doped $\alpha\text{-Fe}_2\text{O}_3$ and $(\text{La}_{1-x}\text{Sr}_x)\text{FeO}_3$ ($x = 0.25$) for a pure n-type and a pure p-type semiconductor, respectively. Their reactivities were measured for the photoproduction of CO_2 and H_2 from a liquid phase phase watermethanol (1:1) mixture. The H_2 photoproduction efficiency from this mixture has been shown to be much higher ($>10^2$ times) than that from water (5), which makes it easier to measure H_2 amounts quantitatively. However, it is possible to compare the H_2 production from this system with that of the water system. Of the materials reported in this paper, the magnesium-doped polycrystalline iron oxide showed the highest efficiency. In particular, we have shown that the existence of spinel phase inclusions in the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure enhances the photocatalytic reactivity, and that the reaction can be regarded as photocatalytic.

Experimental

Catalyst Preparation

Mg-doped α -Fe₂O₃ samples were prepared by using a powder mixture of α -Fe₂O₃ (MCB Reagents, 99%) and MgO (Mallinckrodt, analytical grade) with varied Mg/(Mg + Fe) ratios. Powders were mixed by either dry ball milling or by using a methanol slurry. 500 mg of these mixtures were cold pressed into 0.5" diameter discs at 20,000 Kg/cm² pressure. These discs were sintered in air at temperatures between 1380°C and 1425°C in a vertical tube furnace for 20 hours. The discs were then quenched in water to room temperature.

Nb-doped α -Fe₂O₃ single crystals were grown in this laboratory as previously described by chemical vapor transport using TeCl₄ as a transporting agent (9b). (La_{1-x}Sr_x)FeO₃ (x=0.25) was synthesized using a gel route. Appropriate amounts of different nitrate salts such as La(NO₃)₃·6H₂O (Apache Chemicals), Sr(NO₃)₂ (MCB), and Fe(NO₃)₃·9H₂O (MCB) were dissolved in 180 ml of distilled water. The metal hydroxides were then precipitated using an excess of ammonium hydroxide at pH 12. The resultant gel was aged for 2 hours, then filtered and washed thoroughly with distilled water. The gel was dried in air giving an amorphous xerogel. The xerogel was dried by heating to 280°C for 48 hours. After drying the powder was reground and prefired in air at 800°C for 24 hours. Using this prefired powder, cold pellets were made under 20,000 Kg/cm² pressure. The prefired powders and the pellets were then sintered at 1100°C in a flow of pure oxygen for 72 hours.

X-ray and Electrical Measurements

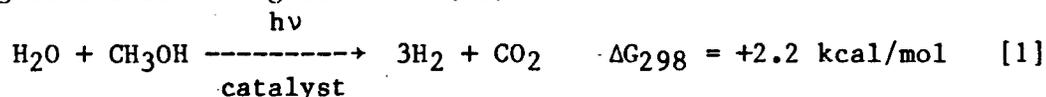
X-ray powder diffraction was carried out on well ground powders of each sample using a Siemens model D500 powder diffractometer equipped

with monochromated CuK α radiation. Measurements of the electrical properties of each sample were carried out using the Van der Pauw four probe technique (17). Ohmic contacts to the samples were made using an indium-gallium eutectic and the ohmicity of the contact was verified by repetitive measurements at current magnitudes between 10 μ A and 100mA. The carrier type was determined by qualitative measurement of the Seebeck voltages.

Catalysis

Powder catalysts for photoreactions were prepared by crushing the corresponding discs or crystals with an agate mortar and pestle. The surface area of each powder was measured using the single point BET method (18) in a Quantasorb surface area analyzer. Pt was deposited on the semiconductor powders by mixing appropriate amounts of the semiconductor powders and Platinum Black (Strem Chemicals) in an agate mortar. The powders were used without further sintering.

Photoproduction of hydrogen was performed by decomposing a water-methanol (1:1) mixture. No reaction occurred in the dark in this system. Under illumination, H₂ and CO₂ gases were obtained as final products according to the following reaction (5a)



All of the experiments were carried out at room temperature. 50 mg of the powder catalyst was introduced into a photoreactor (50 ml pyrex flask) and then the water-methanol mixture (5 ml) was added. The sample reactor was deaerated by a freeze and pump method at least three times. Irradiation of the deaerated system was obtained from a 500 W tungsten halogen lamp and passed through a water filter to alleviate IR heating of the solution. In certain cases colored Corning glass filters were used to provide either

bandgap ($h\nu \geq 2.2$ eV) or sub-bandgap ($h\nu < 2.2$ eV) radiation of the catalysts. Unless otherwise indicated, the light intensity, measured by a calibrated Epply thermopile, was carefully fixed at 100 mW. After the irradiation, the photoreactor was filled with N_2 gas to 1 atm. Gaseous products of the photoreaction were analyzed in a gas chromatograph (Hewlett Packard 5720A) equipped with a thermal conductivity detector. For the determination of H_2 and CO_2 gas production a 1 meter molecular sieve 5A and a 1 meter chromosorb 102 column respectively, were used. N_2 was used as a carrier gas in both cases.

Results and Discussion

Characterization of the Catalysts

The x-ray pattern of the ground crystals of Nb-doped $\alpha\text{-Fe}_2\text{O}_3$ (10b) gave the following parameters: $a = 5.033\text{\AA}$, $b = 13.74\text{\AA}$, in good agreement with the values reported in the literature for the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure (10)(19)(20). Qualitative Seebeck measurements showed that these crystals are n-type semiconductors. The electrical resistivity at room temperature is about $80 \pm 20 \Omega\text{cm}$. In contrast with our Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ sintered discs, the character of which will be described later, these materials are homogeneous semiconductors. We have already shown by magnetic measurements that the low resistivity is not due to Fe_3O_4 spinel phase inclusions but only to a charge compensation mechanism resulting from Nb substitution in the corundum lattice (10a). All the results of the bulk and surface characterization have shown that these Nb-doped $\alpha\text{-Fe}_2\text{O}_3$ crystals are homogeneous n-type semiconductors. The single crystals were ground to powders with a measured surface area of $0.61 \text{ m}^2/\text{g}$ before being used for the photoproduction of H_2 from CH_3OH and H_2O .

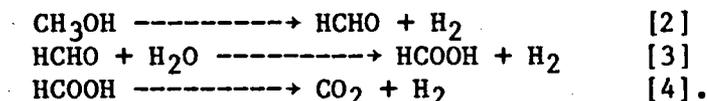
The x-ray patterns of the $(La_{1-x}Sr_x)FeO_3$ ($x = 0.25$) sample were in-

dexed identically with the perovskite type structure (21) in agreement with values reported in the literature (22). The electrical resistivity of these pellets was between 80 to 100 Ω cm, also in good agreement with published data (23). The qualitative Seebeck coefficient indicated a p-type material in agreement with previous results (24). From the BET measurement the surface area of the powder was found to be 2.65 m²/g.

X-ray diffraction patterns of ground sintered discs of Mg-doped α -Fe₂O₃ show the presence of the hexagonal corundum phase of α -Fe₂O₃ and a cubic spinel phase, most likely Fe_{3-x}Mg_xO₄. We have shown that the amount of spinel found in these discs depends mainly on two parameters, the concentration of magnesium and the sintering temperature (13C). Using these considerations we have prepared samples with different ratios of corundum and spinel phases, in order to study the relationship between the spinel phase concentration in the α -Fe₂O₃ corundum structure and the hydrogen production rates from a water-methanol mixture. Table I gives a summary of the characteristics and preparation of these samples including the Mg dopant levels, sintering temperature, resistivity, and measured carrier type. The room temperature resistivity of these iron oxides varies from 10⁶ Ω cm for the pure α -Fe₂O₃ phase (sample 1) to 0.03 Ω cm for the sample with the richest concentration of the spinel phase, 95-100% (sample 4). The qualitative Seebeck voltages show that all the samples are n-type semiconductors. However, photoelectrochemical measurements in aqueous solution showed that the disc electrodes of these materials exhibit photocathodic currents that are characteristic of p-type semiconductors as a result of inhomogeneities in the near surface region (13c). The surface areas of the ground powders determined by BET measurements were 0.19 \pm 0.2 m²/g for all samples.

Hydrogen production from a water-methanol mixture.

We have studied the hydrogen production from a water-methanol mixture using Fe_2O_3 semiconductor powders and their platinum deposited powders. All of the Fe_2O_3 powder systems studied produced H_2 from a water-methanol solution by photoirradiation. CO_2 gas was also observed for the Pt loaded samples after prolonged irradiation. CO and O_2 were not detected. It is known that H_2 and CO_2 arise from the stepwise reactions,



HCHO and HCOOH have been observed as intermediates of the total reaction [1] in TiO_2/Pt systems (5a)(16c). In our experiments, the ratio of CO_2 to H_2 produced was less than 1/3, in every case, supporting the above mechanism.

Because H_2 production is the easiest of the products to measure quantitatively, we have monitored the reactivities of our catalysts through H_2 production. Figure 1 shows the relationships between H_2 production and irradiation time for the Fe_2O_3 powder systems. In this figure, the results for Pt loaded samples are also shown. In all cases, there were distinct differences between samples with Pt loading and without Pt loading. In the case of no Pt loading, the H_2 production rates were quite low. A blank experiment using only Pt Black as a catalyst showed no H_2 evolution. This means that Pt cannot act as a catalyst by itself under these reaction conditions. It is well known that Pt plays an important role in increasing the efficiency of H_2 production in many photocatalytic reactions (5)(6)(12). It is believed that, without the Pt catalyst present many holes and electrons are produced in the valence band and conduction band, respectively, by photoirradiation, but that the recombination rate

of these holes and electrons in the particles is so high that the carriers cannot be used for chemical reactions. On the other hand, Pt loading reduces the recombination rate of electrons and holes by the formation of an accumulation layer in the semiconductor at the metal interface and therefore accelerates the H^+ reduction reaction in addition to H atom recombination catalysis (7). This platinum loading effect occurs even with simple grinding of the Pt with the semiconductor powders and without further sintering after loading.

As is shown in Figure 1, H_2 production from these catalysts both with and without Pt loading increased linearly with the irradiation time in all cases and in no event showed any signs of instability. However, it should be noted that in the cases of the Nb-doped $\alpha-Fe_2O_3$ and the $(La_{1-x}Sr_x)FeO_3$ ($x = 0.25$) it is not obvious that these reactions are photocatalytic since the turnover numbers²⁵ of these systems were still small after long irradiation times (0.69 for Nb-doped $\alpha-Fe_2O_3$ with Pt after 91 hours irradiation and 0.32 for $(La_{1-x}Sr_x)FeO_3$ ($x = 0.25$) with Pt after 89 hours irradiation). However, in the case of the Mg-doped $\alpha-Fe_2O_3$ system, the H_2 production rate (~ 21 nmol/h with Pt) was much higher than the Nb-doped $\alpha-Fe_2O_3$ (2.6 nmol/h with Pt) or the $(La_{1-x}Sr_x)FeO_3$ ($x = 0.25$) (8.3 nmol/h with Pt) and the turnover number²⁵ was greater than 10 after 89 hours of irradiation. This is a good indication that the H_2 evolution from the Mg-doped $\alpha-Fe_2O_3$ can be regarded as a photocatalytic reaction.

Because the Mg-doped system gave the highest turnover frequencies and exhibited the most interesting properties, we concentrated our studies on this material. We measured H_2 production rates from a water-methanol mixture using Mg-doped $\alpha-Fe_2O_3$ samples which had different spinel/corundum ratios (Table I) and were loaded with 10% Pt. Figure 2 shows the correl-

ation between the H₂ production rate and the spinel/corundum ratio of Mg-doped α -Fe₂O₃ with 10% Pt. The H₂ production rate depends largely on the spinel/corundum ratio. Generally, the rate of H₂ production of Mg-doped α -Fe₂O₃ was much larger than that of undoped α -Fe₂O₃ or the Fe_{2-x}Nb_xO₃ (x = 0.02) or (La_{1-x}Sr_x)FeO₃ (x = 0.25) as cited before. From the figure, when the spinel/corundum ratio was 0.37 the H₂ production rate showed its maximum (1.2 μ mol/24hrs). A further increase of the spinel/corundum ratio resulted in a decrease of the H₂ production rate. Previously, we measured the photoelectrochemical behavior of polycrystalline discs of Mg-doped α -Fe₂O₃ against a Pt counter electrode (13C). In that study we also found that the maximum photocurrent was observed when $I_{\text{spinel}} / (I_{\text{spinel}} + I_{\text{corundum}})$ was approximately 0.4, in good agreement with this result. As expected, pure Fe₃O₄ (100% spinel structure) showed no photoreactivity. H₂ gas was not produced by Fe₃O₄ even if Pt was deposited on the powder (Figure 2).

We also measured the light intensity and photoexcitation energy dependence on H₂ production. The results are shown in Figure 3 and Table II. Figure 3 shows that the H₂ production rate increases linearly with light intensity. Table II shows the H₂ production measured for excitation of the Mg-doped iron oxide semiconductor with radiation of sub-bandgap energy and with light of energy greater than the bandgap value (2.2 eV). As expected, the H₂ production rate when bandgap excitation was used was much higher than when only sub-bandgap radiation was used. However, H₂ could also be produced with the sub-bandgap excitation. These results for the H₂ production dependence on photoexcitation energy indicate that H₂ production occurs mainly as a result of bandgap energy irradiation but that H₂ can also be produced with sub-bandgap excitation.

This indicates the presence of deep lying levels within the bandgap. It is known that there are some localized states within the bandgap of α -Fe₂O₃ due to the crystal field splitting of d-orbitals of the cation (26) and from Mott-Schottky measurements (27). Photogenerated carriers from these states may contribute to the density of electrons in the conduction band resulting in the reduction of H⁺ ions to H₂ gas (28). However, further investigations are necessary to understand the influence of energy levels in the bandgap on the photocatalytic reactivity in detail.

Based on these results, we can discuss the photocatalytic nature of these doped iron oxide powders. In all of the powder systems studied H₂ was produced from a water-methanol system, although the reaction rates were small for the Nb-doped Fe₂O₃ and the (La_{1-x}Sr_x)FeO₃ (x = 0.25) systems. It has been known that the flatband potentials of the bulky electrodes of α -Fe₂O₃ are more positive than the H₂/H⁺ level (29), even in the cases of doped materials (10)(11). However, in the case of small particle systems, it has been shown that there is a possibility that the energy level of excited electrons in the Fe₂O₃ particles can be shifted negatively under irradiation (14). The results for H₂ production from our iron oxide powders could be explained by this phenomenon. Among the doped Fe₂O₃ systems studied here, Mg-doped polycrystal particles showed higher reactivity than pure n-type or pure p-type particles. In the case of Fe₂O₃, the existence of the spinel structure in the α -Fe₂O₃ corundum structure enhances the photocatalytic reactivity of α -Fe₂O₃.

Using the band level diagrams shown by Goodenough for α -Fe₂O₃ (26) and Fe₃O₄ (30), combined with optical absorption spectra (19)(31) and theoretical calculations (32), one can see that the conduction band of Fe₃O₄ lies more cathodic (~0.5 eV) than the conduction band of α -Fe₂O₃

assuming that the valence band (O 2p orbitals) edges of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 lie at the same energy when immersed in an aqueous NaOH solution. Thus, the inclusion of the Fe_3O_4 spinel phase in the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure provides the possibility of a small (<0.5 eV) cathodic shift of the conduction band edge of $\alpha\text{-Fe}_2\text{O}_3$, which makes it possible to reduce protons to form H_2 molecules.

As is shown in Table I, the inclusion of spinel phase Fe_3O_4 decreases the resistivity of the catalysts and if this aids the transfer of photo-generated carriers via electron hopping between Fe^{2+} and Fe^{3+} , then the redox reaction kinetics will also be enhanced. Fe_3O_4 , however, is a semi-metal at room temperature (26) and cannot by itself separate electron-hole pairs. Therefore, the further increase of the spinel to corundum ratio the $\alpha\text{-Fe}_2\text{O}_3$ beyond 37% causes a decrease in the reactivity as the material begins to behave more as a semimetal than a semiconductor (Figure 2).

Conclusion

The photogeneration of hydrogen from a water-methanol (1:1) mixture using Nb-doped $\alpha\text{-Fe}_2\text{O}_3$ (pure n-type), $(\text{La}_{1-x}\text{Sr}_x)\text{FeO}_3$ ($x = 0.25$) (pure p-type), and Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ powder suspensions has been examined. The reaction efficiencies of these systems were remarkably enhanced by loading the semiconductors with Pt. Among the systems investigated, Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ showed the highest efficiency. From the linearity of H_2 evolution with the irradiation time, and the turnover number of the reaction, Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ can be regarded as a photocatalytic reactor. In the Mg-doped $\alpha\text{-Fe}_2\text{O}_3$, which contains both the $\alpha\text{-Fe}_2\text{O}_3$ corundum structure and the spinel structure, the H_2 production is largely dependent on the spinel/corundum ratio. The maximum efficiency was obtained with a spinel to corundum phase ratio of about 0.37. The spinel phase existence in $\alpha\text{-Fe}_2\text{O}_3$ may cause

a cathodic shift of the conduction band edge of $\alpha\text{-Fe}_2\text{O}_3$ while the decrease in resistivity of the catalyst may help the mobility and transfer of photo-generated carriers.

With the change of the photon excitation energy range, it was found that this photocatalytic reaction was driven mainly by bandgap (2.2 eV) radiation. However, some localized states within the bandgap also contribute to H_2 production.

Until now, $\alpha\text{-Fe}_2\text{O}_3$ and its related compounds have not been known as suitable materials for photocatalytic evolution of H_2 . However, in this study, we have shown that our multiphase polycrystalline Mg-doped $\alpha\text{-Fe}_2\text{O}_3$ material has the ability to produce H_2 in the photocatalytic process of converting water and methanol to CO_2 and H_2 . Although further study will be needed to understand the reaction mechanism in detail or to increase the efficiency, we found that it is possible to use $\alpha\text{-Fe}_2\text{O}_3$ and related compounds as photocatalysts for solar energy conversion.

Acknowledgements

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25. These turnover numbers were calculated assuming that all of the particles in the reaction flask could be responsible for the photoreaction. However, our irradiation was carried out from one direction (bottom of the flask) and not all of the particles were irradiated at the same time. So, these calculations provide the lowest limit of the real turnover numbers.
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Table I. Characterization of Mg-doped α -Fe₂O₃ samples.

Sample No.	Mg(%)	Sintering Temperature (°C)	Resistivity (Ω cm)	Carrier Type	$\frac{I_{\text{spinel}}}{I_{\text{spinel}} + I_{\text{corundum}}}$	*
1	0	1350	10^6	n	0.0	
2	2	1350	3600	n	0.37	
3	2	1375	4	n	0.55	
4	10	1425	0.03	n	0.95 - 1.0	
5	-	-	-	-	1.0 **	

* This ratio is a qualitative estimation using the integrated step counted intensities of the (220) spinel reflection and the (012) corundum reflection. These values are only an indication of relative intensity.

** Commercial Fe₃O₄ powder (Alfa Products, 99.5%).

Table II. H_2 evolution from a water-methanol (1:1) mixture over Mg-doped Fe_2O_3 under different excitation conditions.

Catalyst: 2% Mg-doped α - Fe_2O_3 with a spinel to corundum ratio of 0.55 and 10% Pt loading

Solution: Water-methanol mixture (1:1) 5 ml

Light source: Tungsten halogen lamp (500W)

Irradiation Conditions	H_2 ($\mu\text{mol}/24\text{hr}$)
no filter	0.54
> 530 nm (Corning Filter #3484)	0.48
> 570 nm (Corning Filter #3480)	0.14

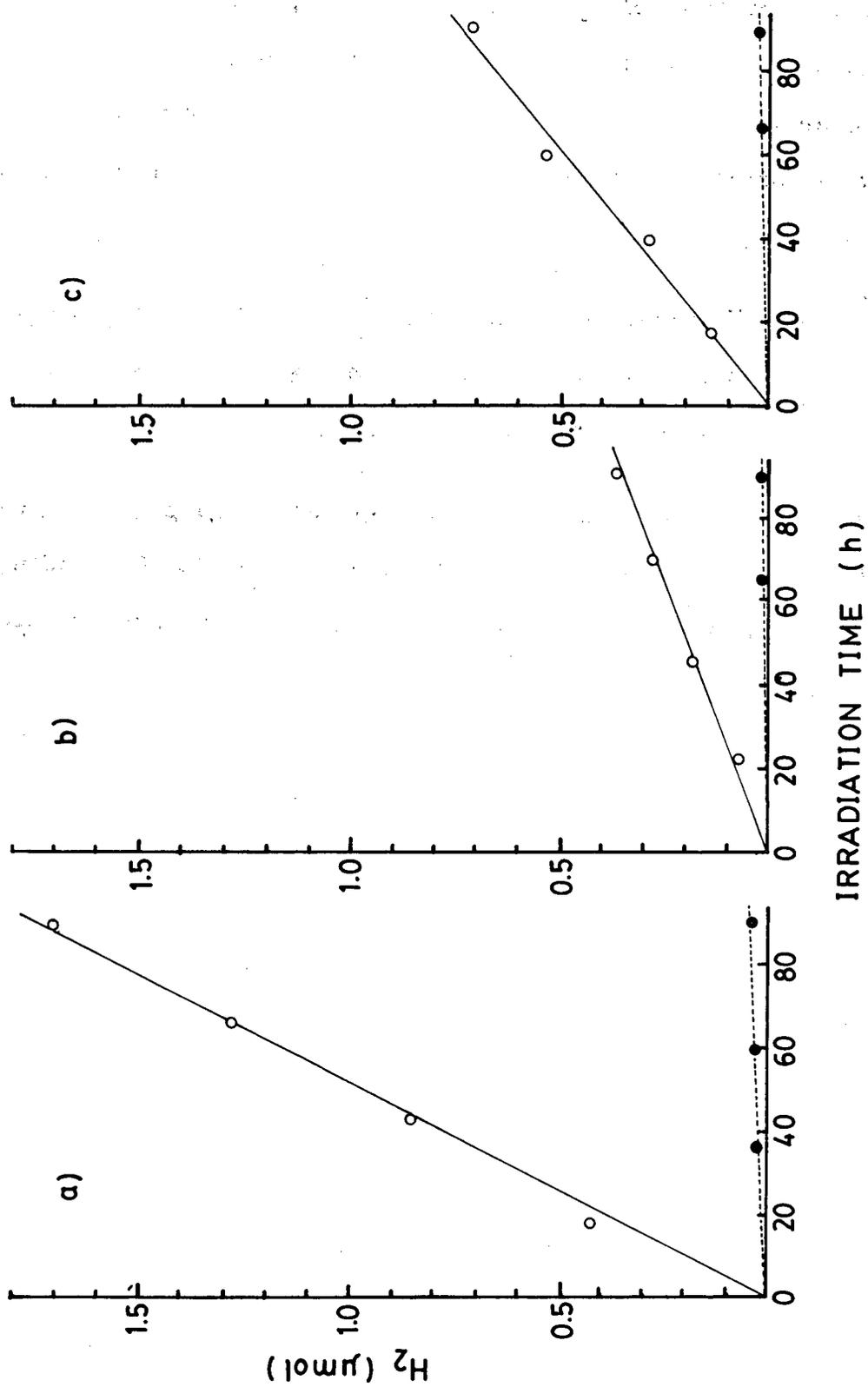
Figure Captions.

Figure 1. Time dependence of H_2 production from a water-methanol mixture (1:1), 5 ml, using a) 10% Mg-doped Fe_2O_3 (sample 4 in Table I) b) Nb-doped Fe_2O_3 c) $(La_{1-x}Sr_x)FeO_3$ ($x = 0.25$). The solid circles represent samples without Pt loading; open circles with Pt loading.

Figure 2. The dependence of H_2 production from a water-methanol mixture (1:1), 5 ml, on the spinel concentration in Mg-doped $\alpha-Fe_2O_3$. All samples have been loaded with 10% Pt.

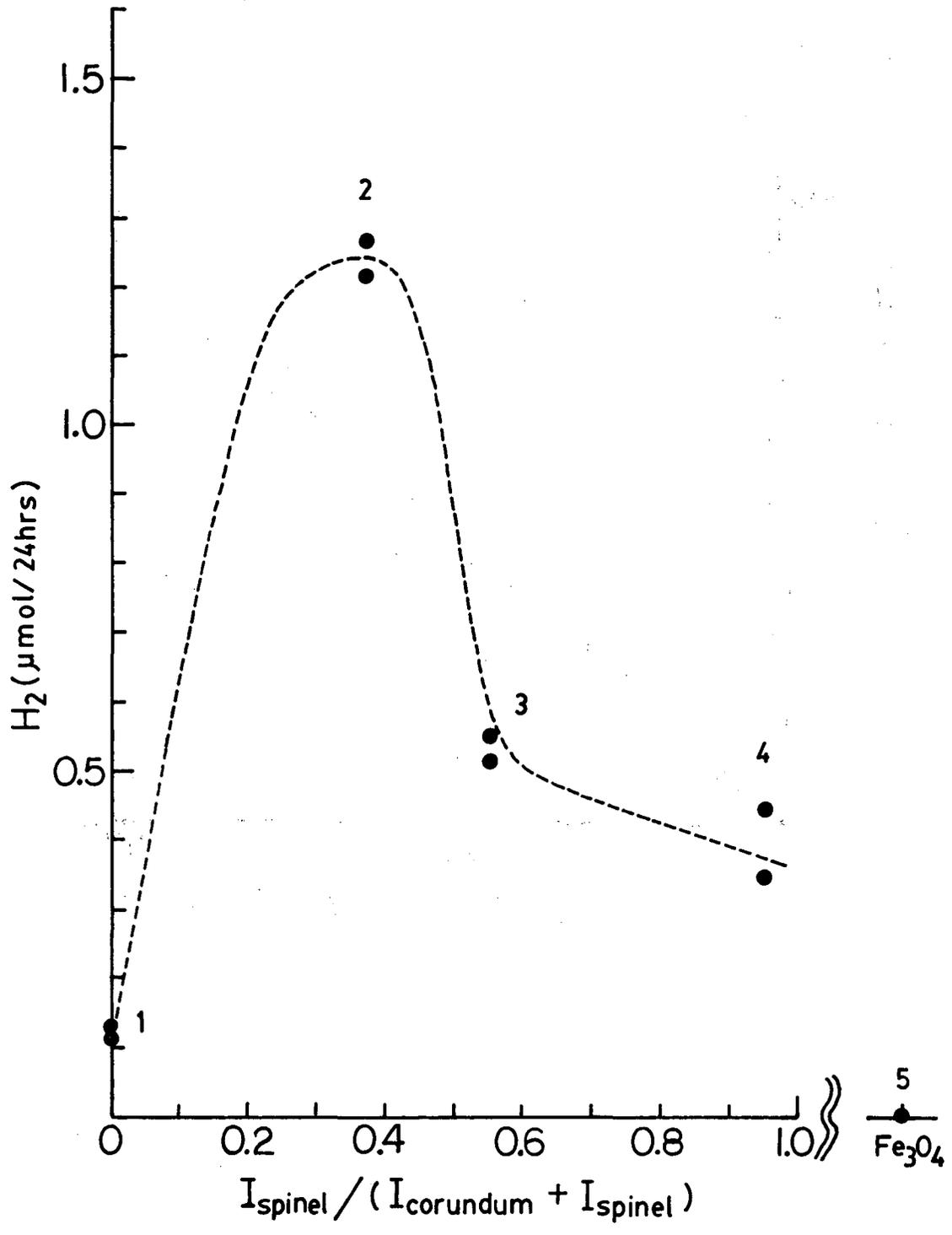
Figure 3. H_2 production dependence on light intensity for a 2% Mg-doped $\alpha-Fe_2O_3$ sample (sample 3 in Table I) with 10% Pt loading. Light intensities were changed by using neutral density Corning filters.

Fig. 1



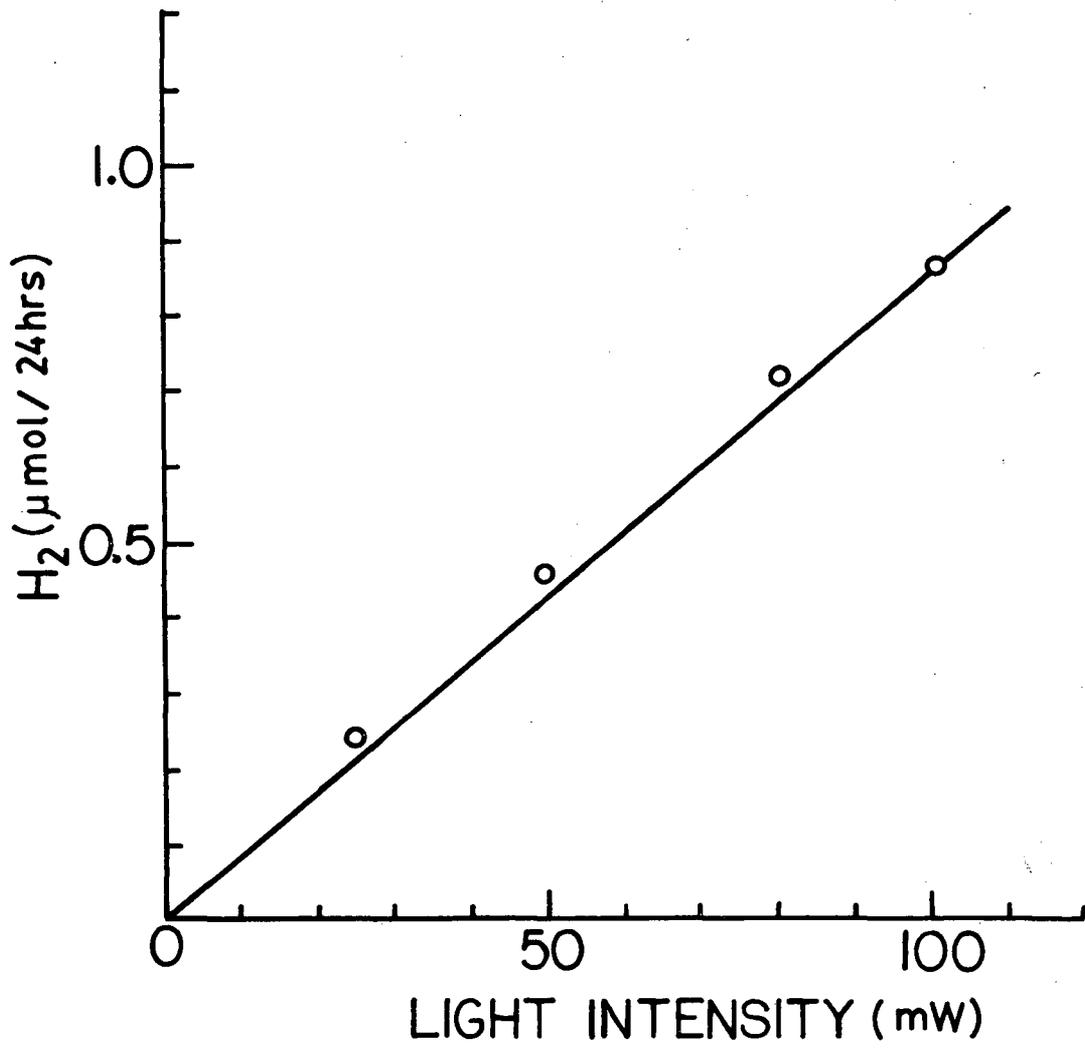
XBL 853-1460

Fig. 2



XBL 853-1461

Fig. 3



XBL 853-1462

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