Pergamon

Int. J. Hydrogen Energy, Vol. 23, No. 9, pp. 741–744, 1998
© 1998 International Association for Hydrogen Energy
Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0360–3199/98 $19.00+0.00

PII: S0360–3199(97)00126–2

ENHANCED PHOTOCATALYTIC H_2 PRODUCTION OVER CdS-ZnS SUPPORTED ON SUPER BASIC OXIDES*

SUPRIYA V. TAMBWEKAR and M. SUBRAHMANYAM†

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad, 500 007, India

Abstract—CdS–ZnS photocatalyst supported on different super basic oxides have been prepared, characterized and tested for H_2 production from a sulfide/sulfite mixture using a halogen lamp source. The results obtained from the 30 wt% Li_2O–MgO support, used photocatalyst gave the highest amount of H_2 production 316 μL/h compared to bear-MgO supported system and the other Li concentrations doped MgO supported CdS–ZnS catalysts. The importance of super basic properties of the used support is substantiated for the high photocatalytic activity obtained. © 1998 International Association for Hydrogen Energy

INTRODUCTION

In our laboratory, recent work has established that a basic support like MgO shows a better performance in H_2 production by CdS–ZnS from a sulfide/sulfite substrate than to γ-Al_2O_3 support which is an acidic oxide [1]. Efforts have been made here to investigate this avenue still further. In base catalysed reactions, reactant acts as acid towards catalyst which acts as base. It seemed therefore of interest to investigate the photodecomposition of H_2S under super basic oxide supported catalysts.

Basic oxides, either of alkali metals or of alkaline earth metals are doped on the support to enhance its properties making it an super basic oxide support. The known base catalyst support now planned is Li-doped MgO and in so far as we are aware, there have been no reports regarding the usage of this system for this proposed test reaction. Within this framework, we have carried out a study on photocatalytic H_2 production studies using different loadings of Li in MgO sample and also La and Pb promoted MgO. The Li^+ doping to MgO introduces an extra charge in the system. Also the effects of CaO, La_2O_3 and Li_2O which are basic supports are also used to compare with MgO supported catalysts.

MgO is a catalytic support which does not contain redox-active metal centres [2]. Basic promoter doping on MgO causes the metal oxides to enter its crystal lattice thus making it attain slight p-type property [3]. The ionic radius of Li^+ is 0.68 and Mg^{2+} is 0.65 hence it introduces more basic sites on the Mg^{2+} ion. Li doping seems to facilitate the separation of photoelectron/holes at the interface and thus enhance the catalytic systems ability to abstract a proton [4]. The basic promoters might be helping in this way to enhance the intimate contact between CdS and ZnS. The semiconductor on an oxide support is said to have an bonding interaction between the interface. Thus, we report here the success in getting enhanced hydrogen yields by using super basic oxide support for the immobilization of CdS–ZnS photoactive material. Also the catalytic activities trend is correlated with the strength of acid/base properties measured for the photocatalysts.

EXPERIMENTAL

Powder catalysts of Li_2O–MgO containing 10, 20, 30, 40 and 50 wt% of Li were prepared from LiOH and MgO (commercial surface areas 170 m^2/gm) and then activated at 450°C in air. CaO, PbO, La_2O_3, Cs_2O, K_2O and Na_2O were prepared by their respective nitrate, carbonate and chloride salts (laboratory grade). Commercial samples of CaO and Sm_2O_3 were used. 10 wt% CdS–ZnS (1 : 1) loadings were given on all the promoted supports, and calcined at 350°C for 3 h. 10 wt% CdS–ZnS (1 : 1) system is chosen as it is giving the best catalytic activity as reported earlier [1].

The photocatalytic experiments were performed in a conventional batch reactor of the type described previously [1]. The UV-visible spectra of the samples were derived from Shimadzu 240 spectrophotometer. SEM photographs of the samples were taken using an Hitachi

---

*IICT Communication No. 3762.

†Author for correspondence.

S-520 and for XRD analysis, a Phillips (Holland) instrument was used with CuK_α radiation. Basicity was measured using benzoic acid titrations.

RESULTS AND DISCUSSION

UV-visible spectra of the samples showed two peaks at 320 nm and 520 nm indicating the presence of CdS–ZnS respectively and no formation of homogeneous solid solutions. A typical UV spectra of CdS–ZnS supported system is given in Fig. 1.

The diffraction studies reveal that supported CdS–ZnS exhibit hexagonal crystal structures. MgO supported samples showed traces of $Mg(OH)_2$. XRD of the Li-promoted samples indicated intense Li_2O, and less intense LiOH peaks, at lower loadings of Li_2O; and at higher loadings of Li_2O, samples show more intense LiOH peaks and less intense Li_2O peaks. Laboratory made CaO exhibiting less activity than CaO (commercial), shows the presence of $Ca(OH)_2$ as well as a cubic structure, in its XRD data.

SEM data of the Li-doped MgO samples exhibits that 10 wt% doped sample has CdS–ZnS partly amorphous but it is spread uniformly on the surface. 20 and 30 wt% unsupported Li_2O–MgO show lot of formation of LiOH which is not seen on supported 20 and 30 wt% Li_2O–MgO catalysts. There is formation of a porous Li_2O on the surface making these catalysts porous and thus exhibiting good activity. At higher loadings of Li_2O on MgO more of LiOH formation is seen on the surface, thus decreasing its activity. Upto 30 wt% Li_2O–MgO; SEM photographs show good flake-like distribution of CdS–ZnS. 50 wt% Li_2O–MgO has more LiOH and CdS–ZnS (phases separated) on the surface attributing to its decrease in photoactivity. 10 wt% K_2O is found to be best promoter for MgO producing 243.7 μmoles/h and its SEM photographs show good distribution of K_2O and MgO without any formation of $Mg(OH)_2$ on the surface. Distribution of photocatalyst over CaO (commercial) surface, is better than CaO used from the laboratory made sample. Promoters on CaO give its surface a porous nature changing its morphology and activity. Li-promoted CaO exhibits good phase separation and crystallites on the surface as is seen by SEM data. Typical SEM Photographs of some of the samples are given in Fig. 2.

Activity data of all catalysts are given in Table 1. Activity and basicity values of some catalysts are correlated in Table 2. 10 wt% CdS–ZnS (1 : 1)/30 wt% Li_2O is exhibiting maximum activity producing 316 μmoles/h. 10 wt% K_2O is found to be the best promoter for MgO producing 243.7 μmoles/h. Commercial CaO is found to be the best support producing 196.4 μmoles/h.

It is observed that basicity is one of the factors determining the activity and the samples show a correlation between the basicity level and the activity level. But in the case of supports like Cs_2O–CaO support, for CdS–ZnS show different activity surprisingly at the same basicity level. For Li_2O–MgO samples there is an increase in photocatalytic activity with increase in basicity. It is also observed that there is no direct correlation between the wt% of promoter and the basicity for some samples. At different wt% of the promoter, the basicity is found to be different for each promoter and support.

CONCLUSIONS

Efforts have been made to develop a CdS–ZnS based super basic oxide support. The support with 30 wt% of Li_2O–MgO having the highest basicity produces maximum amount of H_2. Apart from MgO various other supports have been tried out and CaO is found to be a good support. Promoted CaO samples also exhibit good activity. Currently work is in progress to develop other characterization studies and also develop other basic supports.

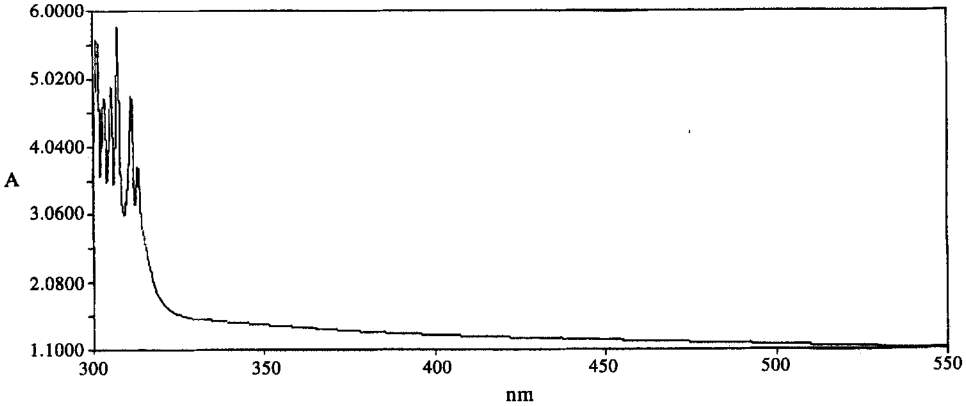
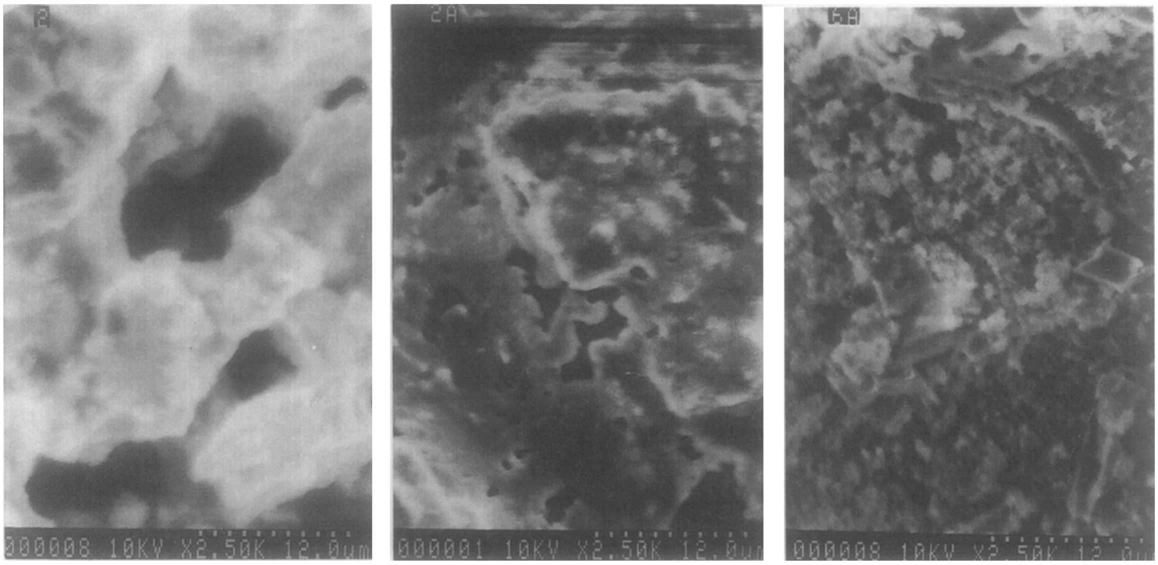


Fig. 1. UV spectra of a typical CdS–ZnS supported photocatalyst.

(a) 20 wt% Li_2O-MgO (b) 30 wt% Li_2O.MgO (c) 50 wt% Li_2O-MgO



(d) 10 wt% K_2O-MgO (e) 10 wt% K_2O-CaO (f) 10 wt% Li_2O.CaO

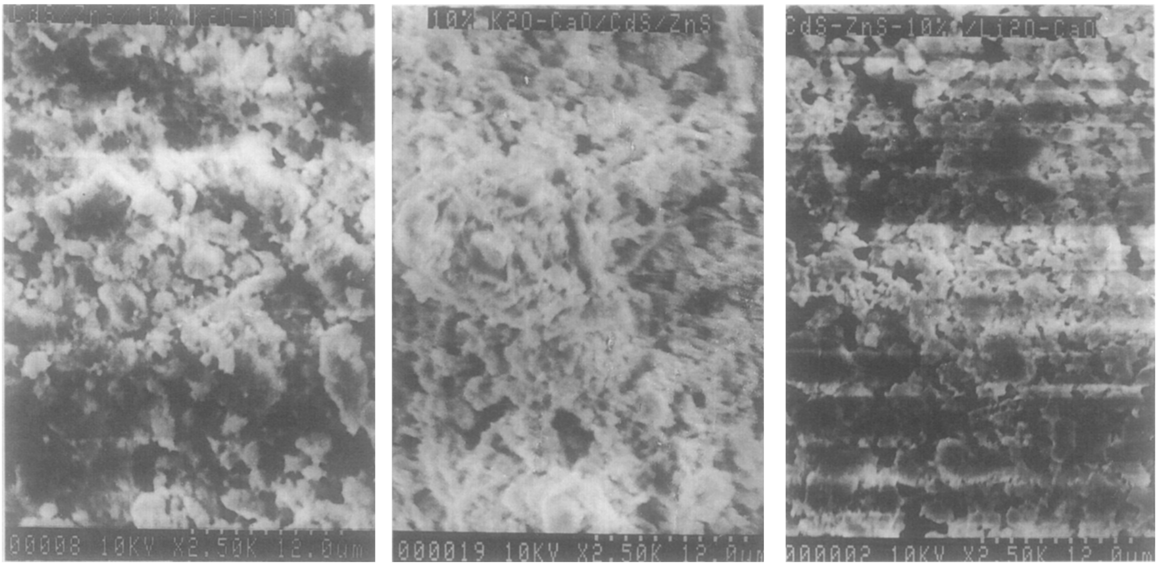


Fig. 2. SEM photographs of 10 wt% CdS–ZnS supported over different supports; (a) 20 wt%Li_2O–MgO, (b) 30 wt% Li_2O–MgO, (c) 50 wt% Li_2O–MgO, (d) 10 wt% K_2O–MgO, (e) 10 wt% K_2O–CaO, (f) 10 wt% Li_2O–CaO.

Table 1. Hydrogen production of 10 wt% of CdS–ZnS (1 : 1) over different supports

Sr. no	Name of catalyst	Amount of H_2 (μmoles/h)
A	Lithium wt% loaded MgO	
1	0	71.4
2	10	178.57
3	20	267.85
4	30	316.96
5	40	294.64
6	50	196.42
7	100	107.14
8	Unsupported (1 : 1) CdS–ZnS	23.0
B	MgO and effect of different promoters (10 wt%)	
1	Li_2O	178.57
2	La_2O_3	28.57
3	PbO	25.0
4	Na_2O	43.3
5	K_2O	243.7
6	Cs_2O	48.2
C	Different supports	
1	MgO	71.42
2	Li_2O	107.14
3	CaO (Lab made)	91.96
4	CaO (Commercial)	196.4
5	La_2O_3	44.64
6	Sm_2O_3	35.2
D	Effect of 10 wt% Li_2O on different supports	
1	MgO	178.57
2	CaO	216.5
E	Li_2O wt% loaded CaO	
1	0	196.4
2	10	228.2
3	20	103.5
4	30	39.2
5	100	107.14
F	K_2O Wt% loaded CaO	
1	0	196.4
2	10	218.7
3	20	169.6
4	30	207.3
5	100	245.5
G	Cs_2O Wt% loaded CaO	
1	0	196.4
2	10	216.5
3	20	193.7
4	30	58.8
H	CaO and different promoters (10 wt%)	
1	K_2O	218.7
2	Cs_2O	216.5
3	Li_2O	228.2

Table 2. Data on basicity and activity of 10 wt% CdS–ZnS supported over different supports

Sr. no.	Name of support	Basicity (mmoles/gm)	Activity (μmoles/h)
1	Bear MgO	1.77	0
2	MgO	1.93	71.4
3	10 wt% Li_2O–MgO	1.92	178.57
4	20 wt% Li_2O–MgO	1.91	267.85
5	30 wt% Li_2O–MgO	1.99	316.96
6	40 wt% Li_2O–MgO	1.97	294.64
7	100 wt% Li_2O	1.86	107.14
8	CaO	1.96	196.4
9	10 wt% Li_2O–CaO	1.99	228.2
10	10 wt% K_2O–CaO	1.97	218.7
11	20 wt% K_2O–CaO	1.94	169.6
12	30 wt% K_2O–CaO	1.96	207.3
13	10 wt% Cs_2O–CaO	1.97	216.5
14	20 wt% Cs_2O–CaO	1.97	193.7
15	30 wt% Cs_2O–CaO	1.97	58.8

Acknowledgements—The author SVT wishes to thank CSIR, New Delhi for Senior Research Fellowship and Dr (Mrs) V. Durga Kumari, for her valuable guidance in basicity measurements.

REFERENCES

1. Subrahmanyam, M., Supriya, V. T. and Reddy, R. P., *Int. J. of Hydrogen Energy*, 1996, **21**(2), 99 and the references therein.
2. Amorebieta, V. T. and Caloussi, A. J., *J. Phys. Chem.*, 1988, **92**, 4576.
3. Zheng, H.-S., Wang, J.-X., Driscoll, D. J. and Lunsford, J. H., *J. Catalysis*, 1988, **112**, 366.
4. Kiwi, J. and Morrison, C., *J. Phys. Chem.*, 1984, **88**, 6146.
5. Supriya V. T. and Subrahmanyam, M., *Proceedings of Eleventh International Symposium on Photochemical Conversion and Storage of Solar Energy (IPS-11)*, July 1996, PC-20, 161, held at Bangalore, India, 1996.
6. Supriya V. T. and Subrahmanyam, M. Photocatalytic production of H_2 from H_2S, an energy bargain. *Int. J. of Hydrogen Energy* (in press)
7. Supriya, V. T., Santosh Reddy, G. Durga Kumari, V. and Subrahmanyam, M., *Proceedings of 13th National Symposium on Catalysis*, held at Dehradun, India, April, 1997.