



PHOTOCATALYTIC H₂ PRODUCTION WITH CdS-BASED CATALYSTS FROM A SULPHIDE/SULPHITE SUBSTRATE: AN EFFORT TO DEVELOP MgO-SUPPORTED CATALYSTS

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Abstract—CdS-based photocatalysts supported on MgO and γ -Al₂O₃ have been prepared, characterized and tested for dihydrogen evolution from a sulphide/sulphite substrate using a halogen lamp source. The effect of precursor salt for CdS preparation, the optimum loading of CdS on the support and the concentration of the catalyst in 50 ml of solution have been investigated. The effect of adding to CdS a semiconductor ZnS–Ag₂S and catalytic materials like Pt and RuO₂ have also been studied. The results obtained from the basic nature of MgO support are compared with the acidic nature of Al₂O₃ support. The importance of the acid–base properties of the support is substantiated by modifying the Al₂O₃ support with base materials like CaO/BaO. Thus, the effect of the acid–base properties of the supports is highlighted.

INTRODUCTION

At the current state of the art, many thermal, thermochemical and electrochemical processes for the conversion of H₂S and S are still difficult to justify in economic terms. Recently, increased attention has been given to photocatalytic decomposition of H₂S into dihydrogen and S in the form of the thiosulfate ion [1–12]. The industrial feasibility of a chemical process depends on many factors of a technological and economic nature. For instance, process is operated in batch, continuous flow, fixed-bed, and particle suspension flow systems etc. Traditionally, in thermal catalysis, the production of various technologically and economically viable catalysts is based upon supported catalysts. Immobilization of the photocatalysts on a solid bed was used in the literature for testing the S²⁻/SO₃²⁻ sacrificial agents in obtaining H₂ evolution [7–9]. Sato *et al.* [8] reported the ZnS–CdS mixture, incorporated into the interlayers of clay, has been found to give more hydrogen in the presence of sulphide/sulphite solution when compared with the bulk mixed chalcogenide system. Furthermore the Al₂O₃ supported mixed semiconductor catalyst ZnS–CdS has shown an improved rate of photohydrogen production for water decomposition [13]. Borrell [1] and other co-workers discussed CdS-based semiconductor catalytic activity for photohydrogen production from sulphide/sulphite sacrificial agents. The effects of adding

TiO₂, Cu₂S and a catalytic material Pt or RuO₂ to CdS have been considered. The technique of preparation of photocatalysts is crucial for a higher yield of product. Thermal treatments in the presence of air or H₂S and chemical or photo etching of the semiconductor catalysts play a crucial role. Furthermore, it is well known that the acid–base properties of catalysts are important in many catalytic reactions, e.g. polymerization, cracking, dehydration, alkylation, halogenation and dehydrogenation [14]. There is a substantial body of literature on the subject of photoelectrochemical conversion of sulphide/sulphite solution to H₂. However, no published data about the acidic or basic nature of the support.

Many CdS-based systems have been extensively studied as bulk semiconductor materials only, not on supported systems. The traditional view of an immobilized semiconductor rests without interaction with the immobilizing agent, whereas the semiconductor on an oxide support may, in many instances, have a bonding interaction between the interface. The understanding of these systems with regard to catalytic activity data has been found necessary. Thus, there is a need for a lot of research into photocatalytic systems to extend several aspects of thermal catalysis principles. With this in mind, in this work, a basic oxide, MgO, and an acidic oxide, Al₂O₃, are chosen for use as supports for CdS-based catalysts for testing the sulphide/sulphite substrate as a sacrificial agent. This approach to the development of systems would take care of the problem of the cost factor

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of the active component, a good dispersion of the active material over a high-surface-area inert solid which forms a heterojunction for electron-hole separation.

EXPERIMENTAL

We used bulk CdS prepared in our laboratory as well as a sample from Aldrich. Etching treatments as reported earlier were carried out to get stoichiometrically pure CdS powder without a CdO fraction [15]. Irradiations were carried out in a Pyrex 100 ml glass vial, equipped with a water jacket and in a closed vessel with a septum arrangement, containing 50 ml solutions (invariably 1.0M Na₂S, 0.1M Na₂SO₃) with 500 mg of catalyst. The suspensions were de-aired with N₂ for 30 min to prevent the uptake of photogenerated electrons by dissolved oxygen. The air space above the solution in the reactor was flushed with N₂ for 1 h in each experiment. A 250 W halogen lamp was used for illumination. Hydrogen gas was detected by gas chromatography using a carbo sieve 5 Å column and N₂ as a carrier gas. The photogenerated dihydrogen was quantified by taking gas samples through the reactor septum (often tested for every repeated interval) and analyzed by a GC calibration curve. Results were reproducible in each case to within 10%.

CdS-based semiconductor photocatalysts were prepared using a conventional impregnation technique. Different precursors and different loadings of active components were used by mixing or co-precipitation methods over MgO and Al₂O₃ supports. The MgO used was kindly supplied by Martin Martia Magnesia, U.S.A., having a surface area of 170 m²/g. The Al₂O₃ was from Harsha and of surface areas of 170 m²/g. Samples of CdS were precipitated from aqueous solutions of Na₂S/(NH₄)₂S and Cd(NO₃)₂, Cd(CH₃COO)₂, CdCl₂ and CdSO₄. Other metal sulphides of Ag and Zn were co-precipitated with CdS using the required amount of metal nitrate. The modified Al₂O₃ support with CaO/BaO was prepared by impregnation of the respective nitrate salts and decomposition in air at 450°C for 5 h. Hexachloroplatinic acid (H₂PtCl₆) was used for the platinumization and RuCl₃ · 3H₂O as the starting material for RuO₂. The chalcogenide catalysts were activated for 1 h in air and 2 h in N₂ at 350°C before use [16]. The sample preparation of metalized catalysts has been described earlier [7,10]. The u.v.-visible spectra of the samples were derived from a Shimadzu 240 spectrophotometer. SEMs of the samples were taken using an Hitachi S-520 and for XRD analysis, a Philips (Holland) instrument was used with Cu K_α radiation.

RESULTS AND DISCUSSION

The diffraction studies reveal that supported CdS has a hexagonal crystal structure. In the mixed ZnS-CdS catalysts, the ZnS also has a hexagonal crystalline structure as is shown by CdS. It is known that ZnS-CdS does

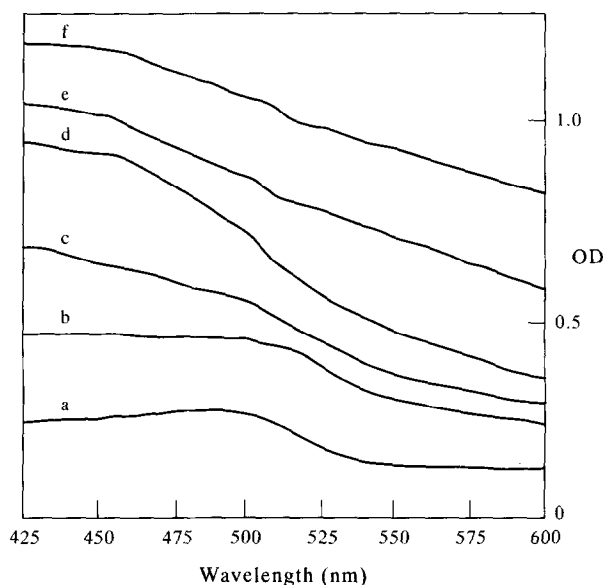


Fig. 1. The u.v.-visible absorption spectra of CdS-based MgO and γ -Al₂O₃ supported catalysts. (a) 10wt% CdS/MgO; (b) 10wt% CdS/ γ -Al₂O₃; (c) 10wt% (ZnS-CdS)/MgO (1:1); (d) 20wt% (ZnS-CdS)/MgO; (e) 10wt% (ZnS-CdS)/ γ -Al₂O₃; (f) 2.5wt% Ag₂S-10wt% (ZnS-CdS)/MgO (1:1).

not form a solid solution of the mixed sulphides [8]. In Ag₂S, ZnS-CdS supported MgO samples were of hexagonal structure, but also some mixtures showed traces of cubic structured particles. It was found that samples containing more hexagonal particles gave better efficiency for hydrogen production [15]. The band-gap energetics (Fig. 1) of CdS and the ZnS-CdS mixture over the supported MgO and Al₂O₃ catalysts are 2.0–2.3 eV when compared with normal crystalline bulk CdS and mixed ZnS-CdS materials which are in the range 2.4–2.8 eV [17]. Tables 1–3 summarize the hydrogen evolution results obtained with a sulphide/sulphite mixture. Other researchers have shown that the addition of sulphite makes the cleavage of H₂S more efficient because the sulphite serves as a sink for the S atoms formed, yielding a thiosulphate [5,14].

Table 1. Dihydrogen formation rate (μ mols/hr) from a sulphide/sulphite sacrificial agent

(a) Cadmium salt precursor effect for CdS/MgO catalyst

Sample	Precursor of CdS used over MgO	H ₂ formation (μ mol/h)
1	Cd(CH ₃ COO) ₂ + Na ₂ S	8.0
2	CdSO ₄ + (NH ₄) ₂ S	8.9
3	CdCl ₂ + Na ₂ S	22.3
4	Cd(NO ₃) ₂ + Na ₂ S	49.1

Table 1. (continued)
(b) Cadmium sulphide loading over MgO support

Sample	Amount of CdS in wt% loading over MgO	H ₂ formation (μmol/h)
1	2	—
2	5	—
3	8	4.0
4	10	49.1
5	15	20.0
6	20	4.4

(c) Effect of concentration of CdS/MgO in 50 ml solution

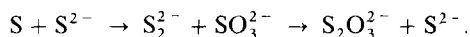
Sample	Concentration of CdS/MgO catalyst in mg	H ₂ formation (μmol/h)
1	50	0.0
2	100	22.3
3	200	29.4
4	300	44.6
5	500	49.2
6	750	37.0

Solution: 1.0M Na₂S + 0.1M Na₂SO₃.

Table 2. Hydrogen production with CdS-based semiconductors over MgO-supported catalysts

Sample	Amount of H ₂ evolved (μmol/h)
1. 10wt% CdS	49.1
2. 10wt% ZnS	0.4
3. 10wt% ZnS: CdS (1:1)	71.4
4. 20wt% ZnS: CdS (1:1)	93.7
5. 10wt% ZnS: CdS (0.17:0.83)	25.0
6. 10wt% Ag ₂ S: 10wt% ZnS: CdS (1:1)	82.4
7. 0.5wt% Pt: 10wt% CdS	140.0
8. 2wt% Pt: 10wt% CdS	61.6
9. 2wt% Ru: 10wt% CdS	82.5

Solution: 1.0M Na₂S + 0.1M Na₂SO₃; amount of catalyst = 500 mg; lamp source = 250 W halogen lamp. Unsupported, laboratory made CdS semiconductor gave 13.3 μmol/h of hydrogen.



The thiosulphate ions result in the regeneration of sulphide ions and help more constant hydrogen production.

In Table 1(a), catalysts containing CdS prepared with different precursors are given. Cd(NO₃)₂ was found to be the best precursor salt. In Table 1(b), the effect of CdS loading on the MgO-supported system is shown. The better yields of hydrogen were found to be at 10wt% CdS. In Table 1(c), investigation was on the influence of catalyst concentration in the solution on the hydrogen production rate. Hydrogen production increased with increased amounts of catalyst concentration up to 500 mg in 50 ml i.e. 10 mg ml⁻¹. Raising the catalyst concentration to 12.5 mg ml⁻¹ reduced the H₂ produc-

Table 3. Hydrogen production with CdS-based semiconductors over Al₂O₃ and CaO/BaO modified Al₂O₃ supported catalysts

Sample	Amount of H ₂ evolved (μmol/h)
1. 10wt% CdS	14.7
2. 10wt% ZnS	—
3. 10wt% ZnS: CdS (1:1)	18.7
4. 0.5wt% Pt: 10wt% CdS	145.0
5. 2wt% Pt: 10wt% CdS	63.0
6. 2wt% Ru: 10wt% CdS	22.3
7. 10wt% CaO + 10wt% CdS	7.4
8. 15wt% CaO + 10wt% CdS	14.7
9. 20wt% CaO + 10wt% CdS	22.4
10. 10wt% CaO + 10wt% ZnS-CdS	33.4
11. 15wt% CaO + 10wt% ZnS: CdS	55.8
12. 20wt% CaO + 10wt% ZnS-CdS	64.8

Solution: 1.0M Na₂S + 0.1M Na₂SO₃; amount of catalyst = 500 mg; lamp source = 250 W halogen lamp. Laboratory made, unsupported CdS semiconductor gave 13.3 μmol/h of hydrogen. Al₂O₃ supported catalysts (Samples 7–12) are CaO/BaO-modified samples.

tion from 49.2 to 37.0 μmol/h. In fact, at higher concentrations, H₂ production decreased faster with time. With these observations, most of the following experiments were carried out with the Cd(NO₃)₂ precursor for CdS at 10wt% loading with 500 mg of catalyst sample suspended in 50 ml of solution of 1.0M and 0.1M S²⁻ and SO₃²⁻ ions, respectively.

From the results obtained in Table 2, it is seen that naked CdS particles produce hydrogen at a rate of 13.3 μmol/h with the aforementioned optimizations. However, MgO-supported CdS leads to an increase in the value, i.e. 49.1 μmol/h of H₂. Furthermore, it has been shown in the literature that the effect of the addition of other semiconductors to CdS appears to be good [8,13]. The charging of the semiconductor phases give rise to the formation of an electric field at the heterojunction. Thus, a MgO-supported mixed semiconductor ZnS-CdS catalyst showed a rate of 93.7 μmol/h of hydrogen, which is a significant rate of hydrogen from S²⁻/SO₃²⁻ without assistance of a noble metal. To compare the results from these systems, the ZnS-CdS mixed semiconductors were used at two loadings and compositions with a view to increasing the efficiency of hydrogen production. The bulk ZnS-CdS mixture also produced an increase in hydrogen production over pure CdS to a few orders of magnitude according to other workers over unsupported chalcogenide catalysts [13]. In addition, the incorporation of Ag₂S into the ZnS-CdS semiconductor mixture supported over MgO was also found to be efficient for hydrogen production. The treatment of CdS with Ag₂S can result in an expansion of the photocatalyst's spectral sensitivity.

The result obtained over an Al₂O₃ support in Table 3 show that, in comparison with MgO-supported systems, the hydrogen evolution is reduced by more than a factor of three. However, here the 10wt% Al₂O₃-supported CdS catalyst showed considerable activity only after platiniz-

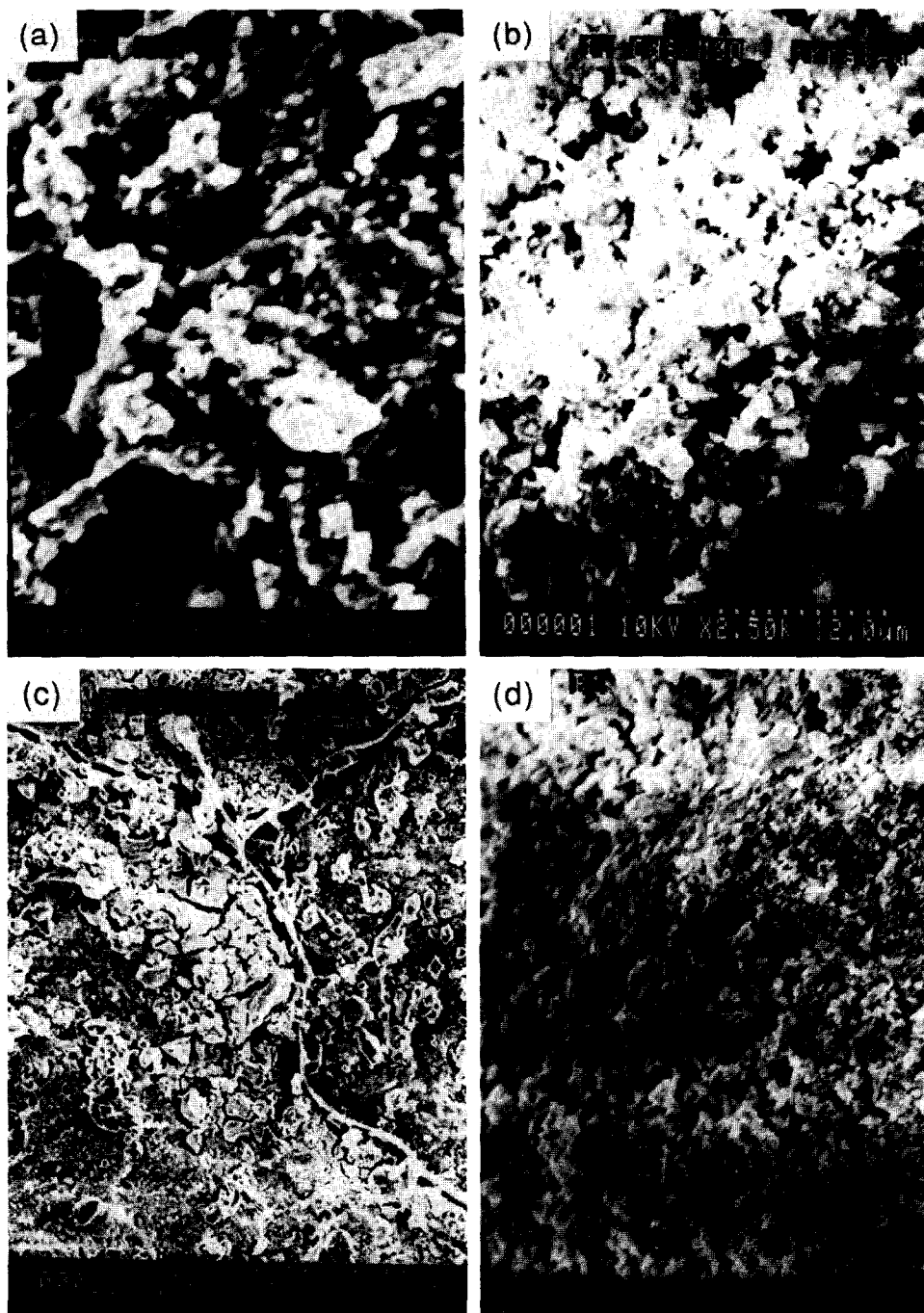


Fig. 2. SEM photographs comparing the migration of CdS particles over MgO, Al₂O₃ and modified Al₂O₃ support, with the corresponding irradiated powders. (a) Laboratory CdS made sample; (b) 10wt % CdS over MgO; (c) 10wt % CdS over Al₂O₃; (d) 10wt % CdS over 10% CaO-modified Al₂O₃.

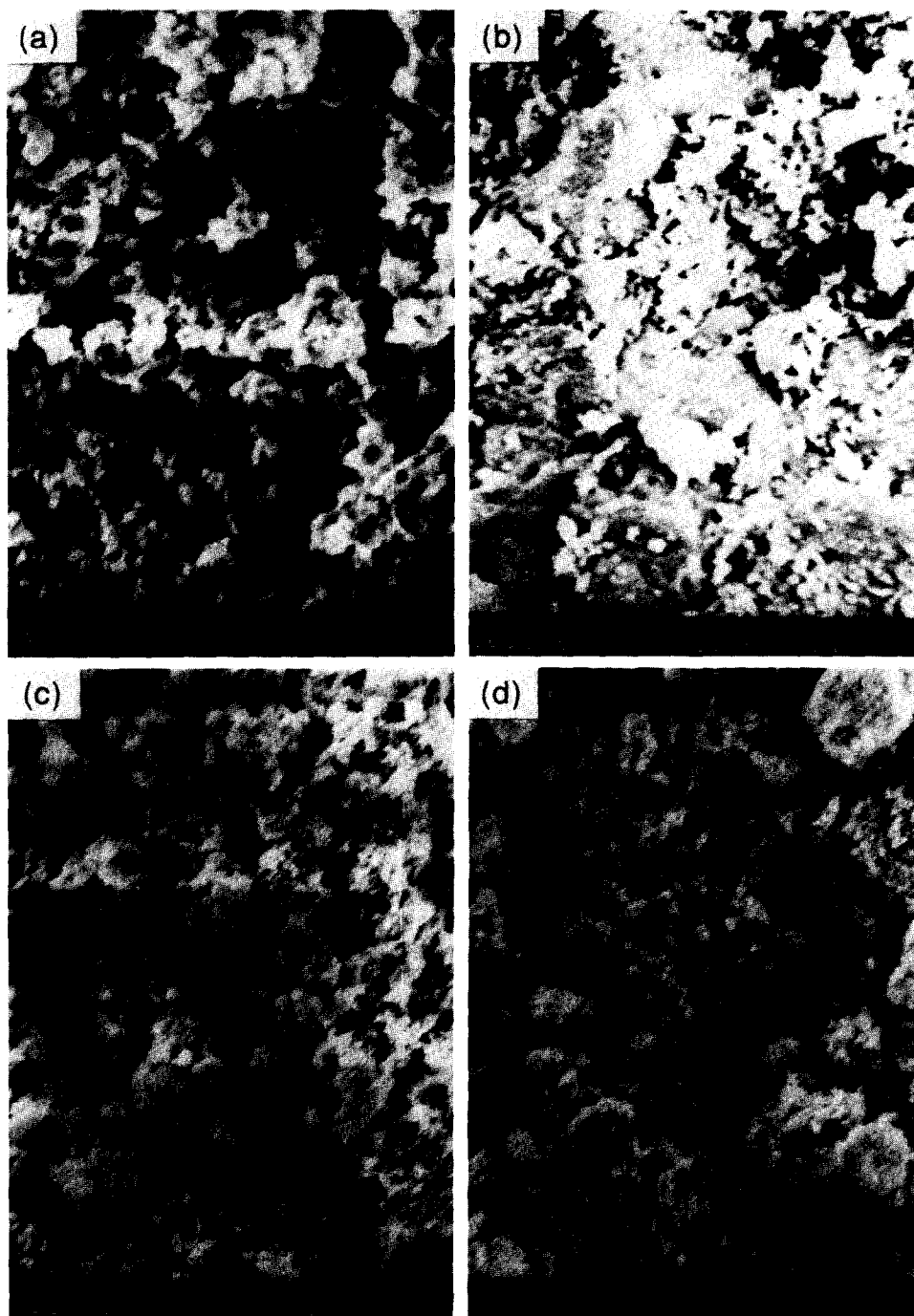


Fig. 3. SEM photographs comparing the migration of 10wt% ZnS-CdS (1:1) with MgO, Al₂O₃ and modified Al₂O₃ supports, with the corresponding irradiated powders. (a) 10wt% ZnS-CdS over MgO; (b) 10wt% ZnS-CdS over Al₂O₃; (c) 10wt% ZnS-CdS over 10% CaO modified Al₂O₃; (d) 10wt% ZnS-CdS over 15% CaO-modified Al₂O₃.

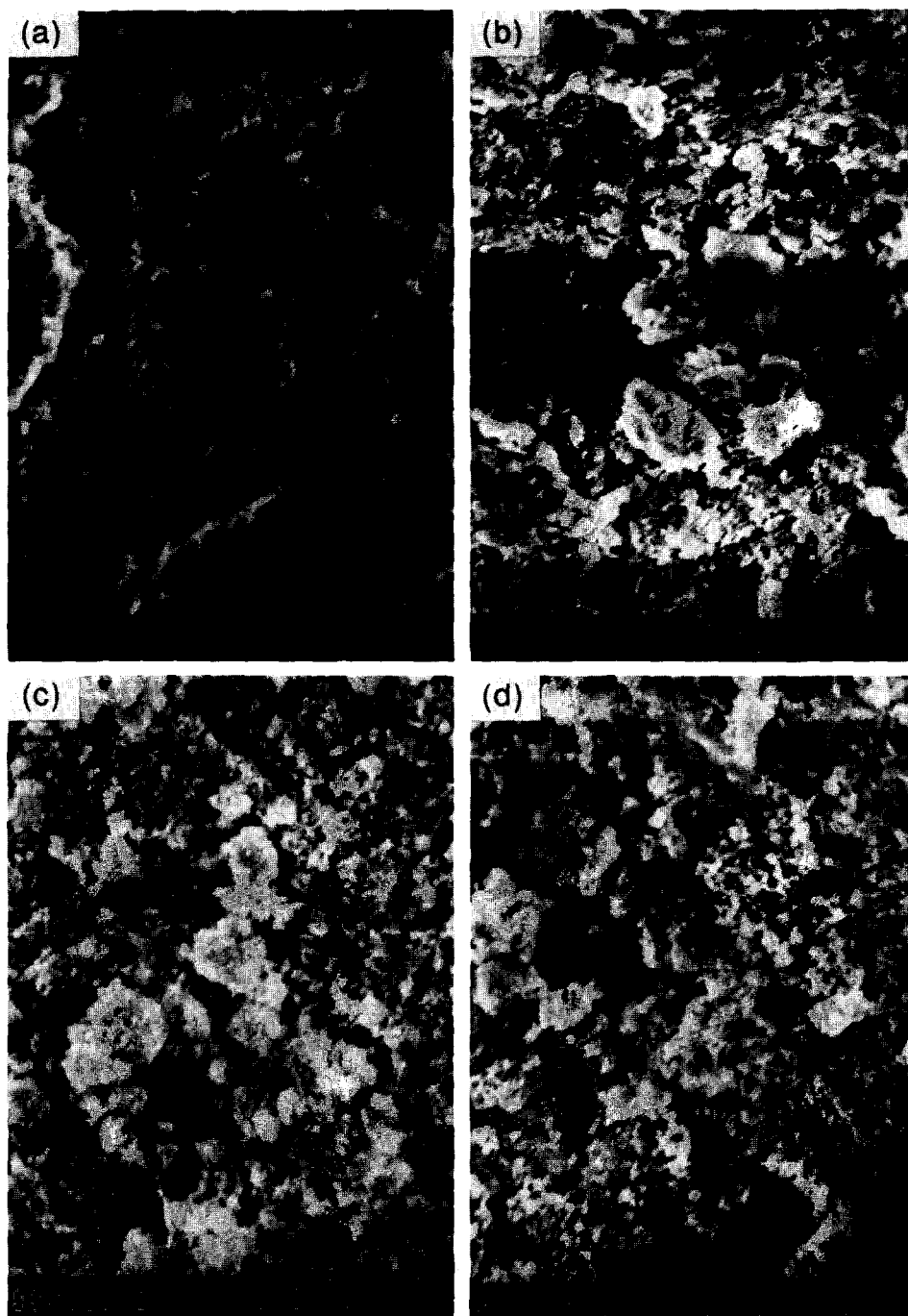


Fig. 4. SEM photographs comparing the migration of Pt on 2.5wt% CdS–10wt% Ag₂S (ZnS–CdS) (1:1) over MgO and Al₂O₃ supports with the corresponding irradiated powders. (a) 0.5wt% Pt 10wt% CdS/MgO; (b) 0.5wt% Pt 10wt% CdS/Al₂O₃; (c) 2.5wt% Ag₂S 10wt% ZnS–CdS/MgO; (d) 2.5wt% Ag₂S 10wt% ZnS–CdS/Al₂O₃.

ation, but not with ZnS doping. The results of hydrogen production over ZnS supported by Al₂O₃ tested separately are similar to the MgO-supported low hydrogen production rate. It is known from the literature for water decomposition that even platinization of Zn accelerates only the back reaction. The activity was not improved by ZnS and Ag₂S doping over Al₂O₃-supported CdS, although the amount of ZnS and Ag₂S was the same as that of the MgO support.

The above observations indicate that intimate contact between the MgO support and the ZnS and CdS particles is necessary for photogeneration of hydrogen. By increasing the ZnS quantity in the CdS, the conduction band is shifted to more a negative, i.e. higher reduction potential and hence produces more hydrogen. In any case, the performance of the ZnS-CdS/MgO system is good, and this indicates that the basic nature of MgO and its intimate contact with the semiconductor/active component favours this synergic effect.

It is known that hydrogen evolution can be enhanced when particles are covered with metals of the platinum group. In this regard, the supported CdS-based catalysts over MgO and Al₂O₃ supports have been checked for catalytic activity after being covered with Pt and Ru. In fact, the effect on hydrogen production of Pt addition to CdS material is a controversial matter [18,19]. Taquikhan reported for these systems that Pt is necessary to ensure a good electron transfer, whereas Ag₂S interfaces directly in the charge separation process or acts as a whole transfer catalyst [20].

From the above results, the importance of the acid-base properties of support is felt to be more important than metallization effects for hydrogen production. In this regard, the data obtained in Table 3, samples 7-9 and 10-12 indicate clearly that the decrease of acidity by modification of Al₂O₃ with CaO/BaO was found to have an enhanced effect for hydrogen production. The modification of Al₂O₃ by CaO from 10 to 20wt% increases the hydrogen evolution of the CdS or ZnS-CdS supported semiconductor. It is also found that either CaO or BaO modification produces the same result.

Solar experiments were also conducted to compare the effect of solar radiation with the radiation from the halogen lamp. The same 100 ml reactor was used in all the experiments. The trend with most of the systems remains the same. The hydrogen evolution can also be further increased by arrangement of the removal of hydrogen from the system. The above-mentioned observations are also substantiated by SEM studies of the samples. The SEM investigations show that the CdS crystallites on the MgO surface become more homogeneous compared with the Al₂O₃-supported samples. The prominent island formations in the case of CdS-based samples over MgO are more comparable than with Al₂O₃-based catalysts. CdS-based catalysts, after modifications of Al₂O₃ with CaO/BaO, are more similar to MgO-supported samples.

CONCLUSIONS

The present investigation explores the development of the use of basic/acidic supports with respect to the photocatalytic H₂S decomposition reaction. The Cd(NO₃)₂ salt precursor for CdS preparation and 10wt% CdS over the support and 500 mg of photocatalyst give higher yields of hydrogen. From the combination of data given in the above-mentioned tables, it can be said that the activity of the supported CdS-based catalysts increases with the basic nature of the support. The addition of ZnS or Ag₂S to CdS also has been shown to be beneficial for hydrogen evolution over the MgO-supported system. On the other hand, the ZnS-CdS/Al₂O₃ material showed lesser activity over the Al₂O₃ support in comparison with MgO. The modification of Al₂O₃ with CaO/BaO gives further evidence of the future selection of basic-supported photocatalysts for development work. A major issue here is the improvement observed for MgO-supported catalysts which is attributed to the basic nature of the support and the good heterojunction developed as suggested by earlier workers. On the whole, it is noted that, inspite of the rather complex behavior of the photocatalytic reactor system, the catalyst showed good activity and trends. The combination Ag₂S·ZnS·CdS/MgO powder formulation was found to be promising. Work in our laboratory is currently under way to investigate various amounts of Li-doped MgO photocatalysts.

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