ELSEVIER

Catalysis Today 69 (2001) 297–305

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Preparation of egg-shell type Al_2O_3-supported CdS photocatalysts for reduction of H_2O to H_2

A.S.K. Sinha*, Namita Sahu, M.K. Arora, S.N. Upadhyay

Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

Abstract

Alumina-supported cadmium sulfide photocatalysts were prepared for the photocatalytic reduction of water to hydrogen using visible light. The activity depends on the nature of interaction between alumina and cadmium and also on the distribution of CdS on the support. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, nitrogen desorption and temperature-programmed oxidation. The impregnation of alumina hydrogel with an ammoniacal solution results into a chemical interaction between cadmium sulfide and alumina and also yields a preferential distribution of cadmium sulfide on the surface which give a better activity to the photocatalyst. The possible role of ammonia in causing the solute segregation to the surface during the drying stage of the catalyst preparation has been explained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalyst; Hydrogen; Solar energy

1. Introduction

Cadmium sulfide has been reported [1–5] as an active photocatalyst for the reduction of H_2O to H_2 using solar radiation. However, for an efficient reduction of H_2O, the photogenerated electrons and holes should not recombine. A possible technique to prevent the charge recombination is to introduce another wide-band semiconductor to the photocatalyst. The second semiconductor not only provides support for the dispersion of the active ingredient but also restricts the charge recombination [6,7] and thus increases the activity of the photocatalysts. However, for this phenomenon to occur, an intimate contact between the two semiconductors is essential [7–9]. However, it is also likely that the support may screen the light away from reaching photocatalyst. Therefore, for a better activity of supported CdS, besides an intimate contact, it should be preferentially distributed on the surface of the support.

In the present work, alumina-supported CdS catalysts were prepared and tested for their activity for hydrogen production from water using visible light. Catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), low-temperature nitrogen desorption and temperature-programmed oxidation. It has been observed that the impregnation of alumina hydrogel by an ammoniacal solution of cadmium sulfate results in the intimate contact and preferential distribution of CdS towards the surface of the alumina support and thus yielding a better activity.

2. Experimental section

2.1. Catalyst preparation

Predried alumina is widely used as a support for catalyst preparation. In the present work also, alumina was used as a support. However, a departure was made and hydrogel of alumina, instead of predried

---

* Corresponding author.

PII: S0920-5861(01)00382-0

alumina, was mixed with the impregnating solutions. A high surface area hydrogel was prepared in the laboratory using the method described by Lippens and Steggerda [10]. The hydrogel was aged for 48 h and then washed with distilled water until it was free of nitrate ions. Alumina-supported cadmium sulfide photocatalysts were prepared by the impregnation technique. The details of catalyst preparation are given below. Unsupported CdS was also prepared.

Catalyst 1. Unsupported cadmium sulfide was prepared by reacting cadmium sulfate with H_2S gas in a fixed-bed reactor at 473 K.

Catalyst 2. Predried alumina (i.e., the hydrogel prepared in the laboratory and at 473 K for 12 h) was impregnated with a requisite amount of ammoniacal solution of cadmium sulfate to yield the final composition by weight as $CdS:Al_2O_3 = 1:2$. The mixture was stirred for 20 h. It was then dried over a water bath with continuous stirring and finally in an air oven at 383 K for 12 h. The dried granules were flushed with nitrogen for 2 h at 473 K to remove any residual ammonia adsorbed on the surface and then reacted with H_2S at 473 K for 5 h in a packed-bed reactor.

Catalyst 3. The only difference in the preparation of this catalyst and catalyst 2 was that, instead of predried alumina, hydrogel of alumina prepared in the laboratory was impregnated.

Catalyst 4. The preparation technique of this catalyst was similar to that of catalyst 2 except that alumina hydrogel was used and it was impregnated with an aqueous rather than ammoniacal solution of cadmium sulfate.

2.2. Activity measurement

The photocatalytic activity of various catalysts for hydrogen production from water was studied in a batch reactor. The photoreactor was 250 ml flat-bottomed flask; one of its sides was also made flat to permit the entry of light through a plane wall. The reactor had a provision for measurement and control of pH and temperature. A 150 W Philips Tungsten-Halogen lamp was used as the light source. The choice of light source was based on the spectral characteristics of the emitted light. No UV or IR filter was used because the spectrum of the light used showed a very negligible emission in the UV range and the use of a Pyrex glass reactor further prevented this radiation from reaching the catalyst. IR radiation can only be absorbed in the form of heat and could increase the temperature of the solution. During experimentation, the temperature could be maintained at the desired value; therefore, the IR filter was also not used.

Two grams of catalyst of size 200 mesh were suspended with a magnetic stirrer in 250 ml of aqueous solution of concentration 0.01 and 0.004 M with respect to Na_2S and Na_2SO_3, respectively. The pH was maintained at 8.6 during the experimentation by adding requisite quantities of NaOH and acetic acid. The temperature was maintained at 333 K and the solution was deaerated by sparging nitrogen for 2 h prior to irradiation. The gas evolved was collected by a water displacement technique and analyzed by a gas chromatograph using a 5 Å molecular sieve column and a thermal conductivity detector. The results showed that the evolved gas was pure hydrogen.

2.3. Catalyst characterization

The BET surface area and pore size distribution of the catalysts were measured by N_2 adsorption at 77 K in a volumetric gas adsorption apparatus. XRD studies were carried out at room temperature using a Philips 1710 X-ray Diffractometer with Cu Kα target of radiation wavelength 1.542 Å. XPS studies were carried out on a Perkin Elmer (Ø 1800, United States) spectrometer using an Mg Kα target. Carbon was used as an internal source for calibration. The temperature-programmed oxidation studies were carried out using Micromeritics Pulse Chemisorb 2705 with a TPD and TPR unit. Samples were placed in a quartz tube and heated at a programmed rate of 15 K per 60 s. Prior to oxidation, samples were heated at 900 K for 5 h in an inert environment of flowing argon gas. For oxidation studies, a mixture of 5.0% oxygen in argon was allowed to flow over the sample at a rate of 0.5 ml s^{-1}.

3. Results and discussion

3.1. Activity

The activity of catalysts as milliliter of H_2 produced for 2 h of irradiation is given in Table 1. It is observed that the supported CdS catalysts exhibited better

Table 1
Hydrogen evolved in 2 h of irradiation

Catalyst	Hydrogen evolved (ml at NTP (g CdS)$^{-1}$)
1	2.0
2	2.7
3	8.1
4	5.9

activity compared to the unsupported CdS. It is in order to mention that the support was expected to prevent charge recombination and to promote better dispersion of CdS. It is likely that these two factors may be responsible for the better activity of the supported catalysts. It is also observed that, in spite of having the same composition, the activities of supported catalysts depend upon the preparation technique. Catalysts 3 and 4, which were prepared by impregnating alumina hydrogel, showed higher activity than catalyst 2 where predried alumina was impregnated. A comparison of catalysts 3 and 4 shows that ammonia in the impregnating solution (catalyst 3) resulted in a better activity as compared to an aqueous solution used for the impregnation (catalyst 4).

3.2. Gas adsorption studies

The physical texture of the catalyst and support was studied by low-temperature nitrogen adsorption. Samples of alumina (Al_2O_3** and Al_2O_3*) were given the same treatments as those adopted for the preparation of catalysts 3 and 4, respectively. Al_2O_3* was prepared by drying alumina hydrogel at 383 K and then heating for 5 h at 473 K whereas Al_2O_3** was prepared by aging gel in ammonia for 24 h followed by drying and heating at the same temperature as Al_2O_3*.

Pore size distribution and cumulative pore volume of radii <150 Å of various catalysts (Table 2) show that the pore volume is dependent on the preparation technique. When alumina hydrogel was treated with ammonia, its total pore volume decreased and the fraction of pores of larger radii increased. The pore volume of catalysts are seen to be substantially less compared to that of the support. A comparison of catalyst 4, which was prepared using an aqueous solution, with Al_2O_3* (alumina subjected to similar treatment), shows that there is a greater decrease in the pore volumes of radii <80 Å. In contrast, the analysis of catalyst 3, which was prepared using an ammoniacal solution, reveals that the fraction of larger pores (>80 Å) has reduced.

3.3. XRD studies

XRD analysis of the catalysts were carried out for the identification of phases and the estimation of crystallite size of CdS. The inter-planer spacing (*d*-value) for each peak was calculated and the peaks were identified as those of CdS, γ-Al_2O_3 and different phases of aluminum hydroxide. Furthermore, an analysis of peaks of CdS revealed that the hexagonal phase of CdS was largely present in all the catalysts. However, a small peak corresponding to cubic CdS was also observed in all the catalysts where ammoniacal solution was used for impregnation.

Mean crystallite size (Table 3) and crystallite size distribution (Fig. 1) of CdS in the supported catalysts were calculated by analyzing the [1 1 0] (i.e., the largest intensity) peak of CdS by the Warren–Averbatch technique [11]. It is evident from Table 3 that the crystallite size depends upon the protocol of catalyst preparation. The use of predried alumina (catalyst 2) instead of its hydrogel had resulted into larger crystallites of CdS. The lower activity of catalyst 2

Table 2
Pore volume of catalysts[a]

Sample	Pore volume × 10^3 (ml g^{-1})			
	30 Å ≥ r_p	30 Å < r_p ≤ 80 Å	80 Å < r_p ≤ 150 Å	r_p ≤ 150 Å
Al_2O_3*	58.0	27.0	13.5	98.5
Al_2O_3**	31.0	29.0	26.0	86.0
Catalyst 3	23.0	12.0	3.0	38.0
Catalyst 4	6.0	11.5	8.0	25.5

[a] r_p indicates pore radius.

Table 3
Mean crystallite size of catalysts

Catalyst	Mean crystallite size (Å)
1	97
2	138
3	68
4	76

is, therefore, attributed to the poor dispersion of CdS. However, in spite of the mean crystallite sizes and crystallite size distributions (Fig. 1) of catalysts 3 and 4 are similar, catalyst 3 showed much superior activity compared to catalyst 4. Therefore, the difference in the activity of catalysts 3 and 4 cannot be correlated with the dispersion of CdS.

3.4. Temperature-programmed oxidation studies

The temperature-programmed oxidation of catalysts used in the present work was carried out to study the interaction between CdS and alumina. The results are shown in Fig. 2. It is observed from this figure that for the unsupported CdS (catalyst 1) the peak in the profile appears at 1000 K. It is also observed from the figure that the oxidation profile of catalyst 3 exhibits separate peaks at 950 and 1000 K. The shift in the oxidation peak to a lower temperature is attributed to the interaction of CdS and alumina. A detailed discussion on interaction of CdS and alumina has been communicated by us elsewhere [12]. Therefore, the appearance of two peaks in the oxidation profile of catalyst 3 may be visualized to be due to different types of CdS dispersion in this catalyst. In the first type, which corresponds to the peak at 950 K, there is a chemical interaction between CdS and alumina, whereas in the second type, corresponding to the 1000 K peak, CdS does not have any chemical interaction with the alumina. This interaction is observed to be absent in catalyst 2, which was prepared by the impregnation of predried alumina. Therefore, it is concluded that the impregnation of predried alumina results in a catalyst (catalyst 2) which has not only a lower dispersion of CdS but also a lack of intimate contact between the support alumina and CdS. The lower activity of catalyst 2 is, therefore, attributed to the above two factors. However, since catalysts 3 and 4 were prepared by the impregnation of alumina hydrogel and therefore the interaction of alumina and CdS to the same extent is expected in both the catalysts, still catalyst 3 showed a better activity compared to catalyst 4.

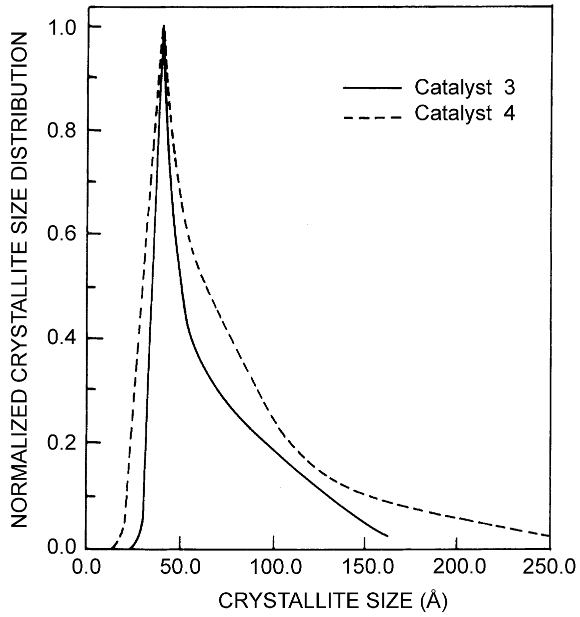

Fig. 1. Crystallite size distribution of catalysts.

3.5. XPS studies

XPS of catalysts 3 and 4 were carried out for surface analysis. The binding energies corresponding to Cd $3d_{5/2}$ and Cd $3d_{3/2}$ peaks coincided well with those reported for CdS [13] (405.0 and 411.8 eV for Cd $3d_{5/2}$ and Cd $3d_{3/2}$, respectively). The binding energies for Al 2p was observed to be 74.6 eV which also matched well with the standard XPS data [14] (74.7 eV for aluminum in aluminum oxide). The XRD analysis, as reported earlier, showed that cadmium was present only as CdS. Although XRD gives bulk analysis, in the absence of any contradictory result, it may be assumed that only CdS is present on the surface as well.

The intensity ratios, as the ratio of peak areas for cadmium ($3d_{5/2}$) and aluminum (2p), of both the catalysts were also calculated. The values were ∞ (no Al peak was observed) and 0.55, respectively, for catalysts 3 and 4. The intensity ratio is a function of dispersion as well as relative concentration of the active ingredient on the surface [15,16]. Thus, a better

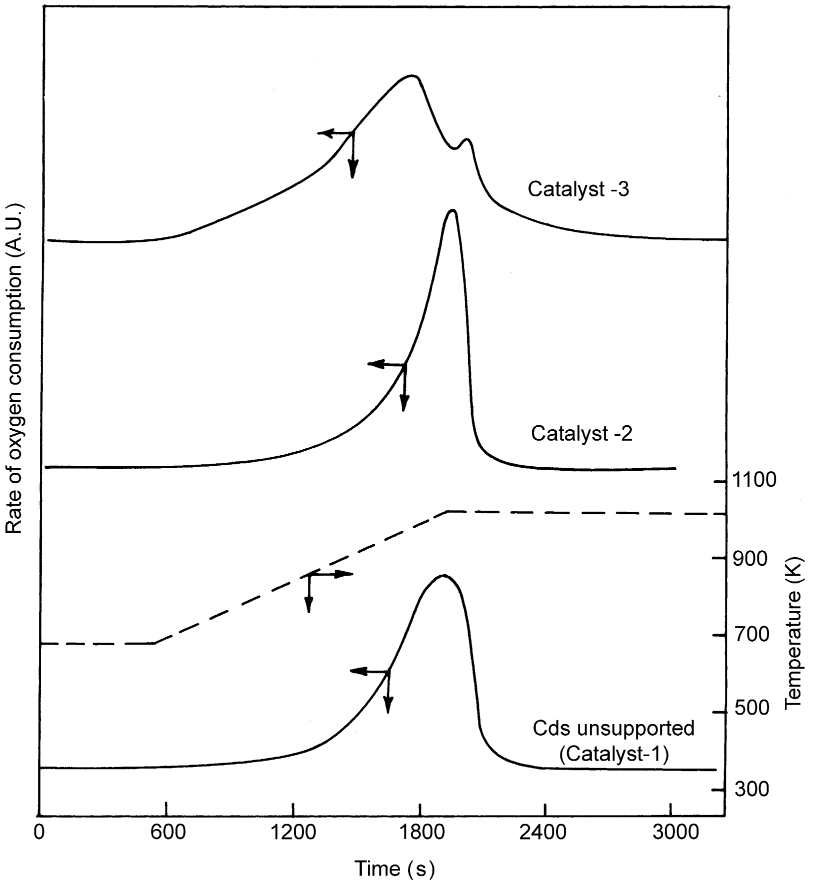

Fig. 2. Temperature-programmed oxidation of catalysts.

dispersion and higher concentration of CdS will yield a higher values of the Cd/Al intensity ratio. It is observed that catalyst 3, where ammonia was used as the impregnating solution, has a higher intensity ratio compared to catalyst 4, where an aqueous solution was used for impregnation. The XRD analysis has shown that catalysts 3 and 4 have crystallites of comparable sizes; hence the large difference in the Cd–Al ratio may be attributed to a higher surface concentration of CdS in catalyst 3 compared to that of catalyst 4. The nitrogen desorption studies, as discussed earlier, also indicated the preferential distribution of CdS on the support in catalyst 3. Therefore, the superior activity of catalyst 3 compared to that of catalyst 4 is due to a higher concentration of CdS on the surface of the catalyst. This difference in activity could not be explained by dispersion or formation of intimate contact between alumina and CdS (cf. XRD and temperature-programmed oxidation results). It is relevant to emphasize that a preferential distribution of active ingredient on or near the surface is desirable for the photocatalytic reactions, since light cannot penetrate deep inside the porous matrix of the support.

The depth profiling of the catalysts was carried out by obtaining XPS results after argon ion sputtering for a desired period of time. Two more samples, i.e., samples 1 and 2 were also analyzed. These samples were prepared by the same method as catalyst 3 but the CdS:Al_2O_3 ratios were 1:10 and 1:5, respectively. The Cd/Al ratios were calculated at different sputtering times and are plotted in Fig. 3. It is observed that the ratio is essentially constant for samples 1 and 2 and

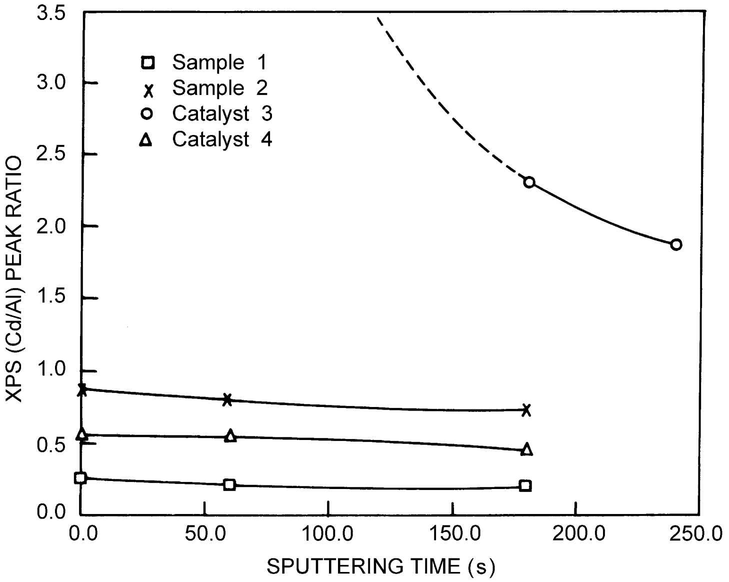

Fig. 3. XPS intensity ratio vs. sputtering time of catalysts.

catalyst 4, whereas there is a noticeable drop in this ratio in catalyst 3. This indicates that catalyst 3 has much greater preferential distribution of CdS towards the surface compared to other samples including even those prepared by ammoniacal impregnating solution (samples 1 and 2).

Cd/Al ratios for different sputtering times of catalyst 3 and samples 1 and 2, all prepared by the same technique, i.e., by the impregnation of aluminum hydroxide gel with an ammoniacal solution of cadmium sulfate but having different compositions, are plotted in Fig. 4. It is observed that the curves are nonlinear and show positive deviations from a linear relationship.

Kerkhof and Moulljn [17] have concluded that when an active ingredient is homogeneously distributed on a support, a linear relation between the intensity ratio and the bulk composition exists, and any change in either the crystallite size or distribution of the active ingredient on the support would show a deviation from the straight line. Therefore, when either the crystallite size becomes small or surface concentration increases or both, a positive deviation will be observed and vice versa. XRD results (not discussed in the present paper) showed that the crystallite size increases with an increase in the loading of CdS. Therefore, the positive deviation, as seen in Fig. 4, indicates that there is a preferential distribution of CdS toward the surface in those catalysts that were prepared using an ammoniacal impregnating solution. Further, this phenomenon becomes more pronounced with an increase in the bulk concentration of CdS.

The preferential distribution of CdS on the surface of catalyst can be explained on the basis of the drying of solid soaked in a solution. The solute segregation arises from the migration and subsequent deposition of the solute during the drying operation. The evaporation of liquid increases the solute concentration near the surface exposed to the drying medium as the liquid evaporates. The solute will also diffuse back into the porous material because of the resulting concentration gradient which tends to reduce the segregation. Further, the liquid evaporation also develops capillary suction, which causes the solution inside the porous material to flow toward the surface exposed to the drying medium. Thus, the capillary flow further increases the concentration at the exterior surface. Because, of small pores of a few angstroms in size, gravitational force is negligible in comparison to the frictional and surface tension forces, natural convective transport

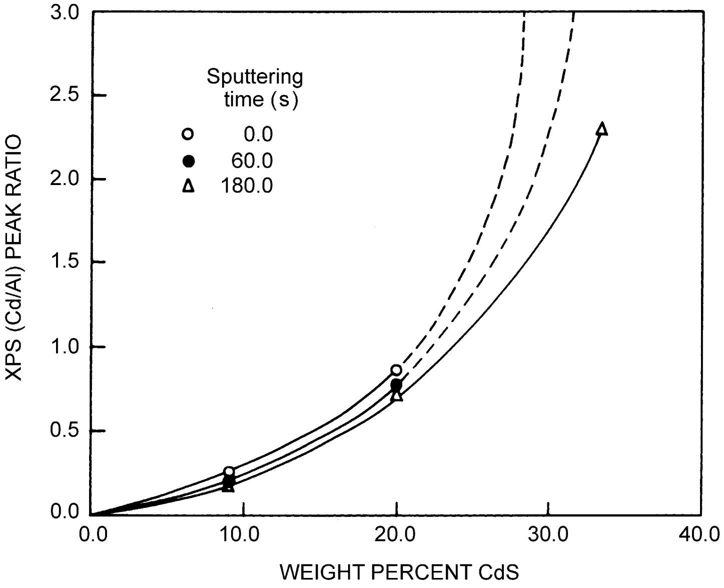

Fig. 4. XPS intensity ratio vs. weight percent of CdS in catalysts.

inside the pores cannot take place. When the solute concentration exceeds the saturation value, crystallization of solute occurs. Thus, the degree of solute segregation shall depend on the relative rates of drying, capillary flow, and diffusion.

Catalyst redistribution during the drying operation may be even more complicated because of the fact that the initial distribution of the solute may not be uniform and further the migrating solute can be adsorbed on the walls of the pores. It is well known that porous materials, such as alumina, silica, etc., have adsorption sites. When a solute dissolved in a liquid fills the pores, some of the solute gets adsorbed on the walls of the pores. Once adsorbed, the solute becomes unavailable for further migration to the surface. Hence, if the concentration of the solute is lower than the adsorption capacity of the support, most of the solute will be adsorbed and its migration to the surface cannot take place. Under such a condition, a uniform distribution of the active ingredient in the catalyst is expected. On the other hand, any solute in excess of the adsorption capacity of the support will remain mobile and migrate to the surface during the drying operation. Thus, a preferential distribution of the active ingredient is more likely.

3.6. Adsorption studies

The results of adsorption studies of aqueous and ammonium solutions of cadmium sulfate on alumina hydrogel are shown in Fig. 5. In both the cases, Langmuir-type isotherms are observed. However, the saturation is reached at a fairly low concentration of Cd^{2+} ions when an ammoniacal solution is used. This may be due to a competitive adsorption of NH_4^+ and Cd^{2+} on the adsorption sites of alumina. As a result only a smaller fraction of sites becomes available for the adsorption of Cd^{2+}. This also means that, for the same concentration of Cd^{2+} in the solution, its adsorption shall be less when ammonia is present in the solution. Therefore, for catalyst 3, which had the same composition as catalyst 4 but was prepared using an ammoniacal solution, more of Cd^{2+} remained in solution during its preparation and consequently migrated to the surface during the drying stage.

The presence of a highly volatile component in the fluid used for impregnation would also significantly affect the transport of the evaporating fluid phase to the surface exposed to the drying medium. Lee [18] has reported that, in the case of impregnation of a dry porous solid, the solution is sucked into the pores, which

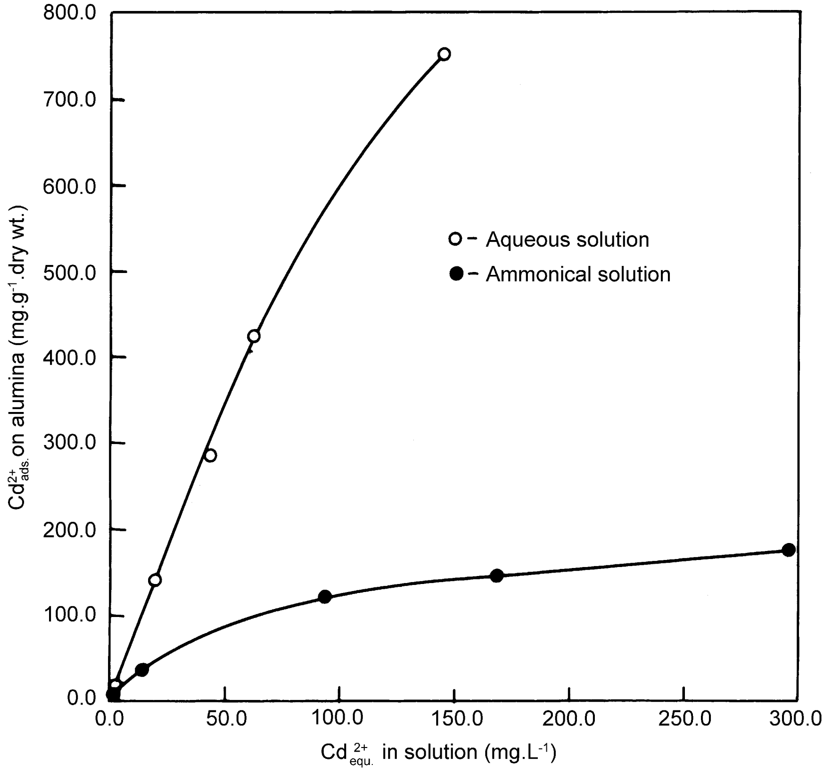

Fig. 5. Equilibrium adsorption of Cd^{2+} on alumina hydrogel.

causes entrapment of air inside the pores. During the drying operation, in addition to the capillary-induced flow, expansion of the entrapped air also causes the liquid column ahead to move to the surface exposed to the drying environment. In this light, the possible role of dissolved ammonia in the solution in causing the preferential distribution of CdS on the surface of alumina may be explained. At the drying stage, the evolution of ammonia will force the solution to the surface. In such an event, the evaporation of liquid will take place from near the surface for an extended period of time, resulting on a higher concentration of solute on the outer surface.

Thus, the higher surface concentration of CdS in catalyst 3 compared to catalyst 4, which has the same bulk composition, is attributed to the presence of dissolved ammonia in the impregnating solution used for the preparation of the former catalyst. Further, the observed difference in the distribution profiles of CdS in catalyst 3 and samples 1 and 2 that were prepared using an ammoniacal solution, could also be explained. It was observed that for low concentrations of CdS its distribution in the catalysts tends to become uniform. This is attributed to adsorption of solute on the wall surface. For the catalysts having low concentrations of CdS, only a small fraction of solute would remain mobile in the solution for the solute segregation to occur yielding a rather uniform distribution.

4. Conclusions

The interaction between support alumina and CdS and the distribution of CdS on the support strongly affects the photocatalytic activity of alumina-supported cadmium sulfide photocatalysts. The use of alumina hydrogel as support promotes a chemical interaction between Al_2O_3 and CdS yielding a better activity. Impregnation of alumina with an ammoniacal solution results in a preferential distribution of CdS on the surface. The NH_4^+ ions present in the impregnating solution compete with Cd^{2+} ions for the adsorption on alumina and also cause a change in the mechanism of drying of the porous support soaked with a solution. For the preferential distribution of CdS on the alumina surface to occur, the concentration of the precursor salt should be in excess of the adsorption capacity of the support.

Acknowledgements

The funding received from the Ministry of Non-conventional Energy Sources, Government of India, New Delhi, India and the All India Council for Technical Education, New Delhi, India is thankfully acknowledged by the authors. NS thanks the Council of Scientific and Industrial Research, New Delhi, India and MKA thanks the Banaras Hindu University, Varanasi, India for providing financial support in the form of fellowships.

References

[1] J.R. Darwent, G. Porter, J. Chem. Soc., Chem. Commun. 4 (1981) 145.
[2] M. Matsumura, Y. Saho, H. Tsubomura, J. Phys. Chem. 87 (1983) 3807.
[3] L. Borrell, S. Cervera-March, J. Gimenez, R.A. Simarro, Sol. Energy Mater. Sol. Cells 25 (1992) 25.
[4] G.C. De, A.M. Roy, S.S. Bhattacharya, Int. J. Hydrogen Energy 2 (1996) 19.
[5] M.K. Arora, N. Sahu, S.N. Upadhyay, A.S.K. Sinha, Ind. Eng. Chem. Res. 37 (1998) 1310.
[6] E. Borgarello, N. Serpone, M. Grätzel, E. Pelizzetti, Inorg. Chim. Acta 112 (1986) 197.
[7] J. Kobayashi, K. Kitaguchi, H. Tsuiki, A. Ueno, J. Chem. Soc., Faraday Trans. 1 83 (1987) 1395.
[8] N. Kakuta, K.H. Park, M.F. Finlayson, A. Ueno, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber, J.M. White, J. Phys. Chem. 89 (1985) 3828.
[9] A. Ueno, N. Kakuta, K.H. Park, M.F. Finlayson, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber, J.M. White, J. Phys. Chem. 89 (1985) 3828.
[10] B.C. Lippens, J.J. Steggerda, in: B.G. Linsen (Ed.), Aspects of Adsorbents and Catalysts, Academic Press, New York, 1970.
[11] C.D. Wagner, in: J.B. Cohen, J.E. Hilliard (Eds.), Local Atomic Arrangements Studied in X-ray Diffraction, Breach Scientific Publishers, Newark, NJ, 1970.
[12] M.K. Arora, N. Sahu, S.N. Upadhyay, A.S.K. Sinha, Ind. Eng. Chem. Res. 38 (1999) 4694.
[13] C.J. Veseley, D.W. Langer, Phys. Rev. B 4 (1971) 451.
[14] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilengerg, Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer, Eden Prairie, MN, 1978.
[15] S.A. Best, R.G. Squires, R.A. Walton, J. Catal. 47 (1977) 292.
[16] A.S. Al-Ubaid, Ind. Eng. Chem. Res. 27 (1988) 790.
[17] F.P.J.M. Kerkhof, J.A. Moulljn, J. Phys. Chem. 83 (1979) 1612.
[18] S.Y. Lee, Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1981.