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Visible Light Induced Hydrogen Evolution on CdS/$K_4Nb_6O_{17}$ Photocatalyst

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The photocatalytic ability of CdS/$K_4Nb_6O_{17}$ photocatalyst for H_2 evolution by visible light irradiation was studied in connection with its structure. CdS/$K_4Nb_6O_{17}$ was prepared by cation exchange reaction of K^+ to Cd^{2+} ions in aqueous $Cd(NO_3)_2$ solution, followed by sulfurization in aqueous Na_2S solution. The catalyst obtained by this procedure showed much higher H_2 evolution activity in aqueous K_2SO_3 solution under visible light irradiation (λ>420 nm) than a physical mixture of CdS and $K_4Nb_6O_{17}$ powders. This result was interpreted as due to more intimate contact of CdS and $K_4Nb_6O_{17}$ in CdS/$K_4Nb_6O_{17}$ photocatalyst, which enabled the efficient transfer of excited electrons. The activity of the catalyst was greatly dependent on the sulfurization condition, with this optimum condition: at room temperature for one week. XRD, EXAFS, TEM, and UV-DRS showed that most CdS particles, ca. 10 nm in diameter, existed on the external surface of $K_4Nb_6O_{17}$, while a small amount of CdS was inferred to be located at the interlayer space of $K_4Nb_6O_{17}$ as ultra fine particles.

Although various kinds of metal oxides have been examined as photocatalysts for hydrogen evolution from water, the wide band gaps (>3.0 eV) of most of them inhibit the utilization of light in the visible region. On the other hand, some sulfides such as CdS possess relatively narrow band gaps, and photoexcited electrons in the conduction band often have potential to reduce H^+ to H_2. For the efficient H_2 evolution, however, modification of CdS by a catalyst such as Pt is necessary. Interparticle electron transfer between different semiconductor powders has been investigated by several workers.

Serpone et al.[1)] observed that the rate of H_2 evolution from aqueous Na_2S or methanol solution over irradiated CdS particles was enhanced by a separately deposited redox catalyst (Pt or RuO_2) on TiO_2 or Al_2O_3 particles. They attributed the enhancement to the electron transfer from the conduction band (CB) of activated CdS to the CB of TiO_2, resulting in the reduction of H^+ to H_2 on Pt or RuO_2.

Sobczynski et al. reported the activity of H_2 evolution under visible light irradiation in methanol solution on mixtures of CdS/SiO_2 with a platinized oxide (TiO_2, ZnO, SnO_2, or WO_3)/SiO_2[2)] and with a WS_2/SiO_2.[3)] In the former system, their interpretation on the mechanism was different from that of Serpone et al. They concluded that the electrons in the CB of CdS were transferred not to the CB of metal oxides but directly to the supported Pt, based on their observations of the independent rate of H_2 evolution from the energy levels of the CB of the oxides; some of the CB's were actually more positive than the redox potential of H^+/H_2.

Spanhel et al.[4)] reported the observation of electron injection from illuminated CdS into attached TiO_2 and ZnO particles without any catalysts such as Pt.

CdS has been prepared in various solid matrices such as Nafion®,[5)] cellulose,[6)] vicor glass,[7)] silica,[8)] and clay,[9)] and exhibits characteristic behaviors in those systems.

The present authors reported that $K_4Nb_6O_{17}$ powder, which had an ion-exchangeable layered structure, photocatalyzed the evolution of H_2 efficiently from aqueous methanol solution without any assistance of other catalysts.[10,11)] Furthermore, suitable modification of $K_4Nb_6O_{17}$ by Pt or Ni enabled the complete decomposition of H_2O into H_2 and O_2 steadily under the band-gap irradiation (3.3 eV).[11—16)] It was also found that H_2 evolved by a mechanical mixture of CdS and $K_4Nb_6O_{17}$ powders under visible light irradiation in an aqueous K_2SO_3 solution.[17)] As illustrated in Fig. 1, we propose that the excited electrons in CB of CdS under visible light irradiation were transferred to the more positive CB and/or surface state of $K_4Nb_6O_{17}$ to reduce H^+ to H_2. This electron transfer between two individual kinds of semiconductor particles only occurred through collisions in aqueous solution. Therefore, the efficiency of H_2 evolution is expected to be enhanced from the mechanically mixed system if more intimate contact between CdS and $K_4Nb_6O_{17}$ is obtained or if CdS is intercalated

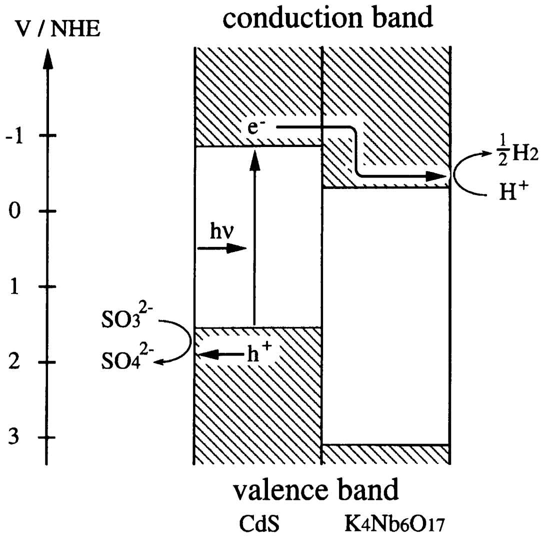

Fig. 1. Schematic diagram of the H_2 evolution caused by electron transfer from CdS to $K_4Nb_6O_{17}$ under visible light irradiation in aqueous K_2SO_3 solution.

at the interlayer spaces of $K_4Nb_6O_{17}$.

In the present work, $CdS/K_4Nb_6O_{17}$ was prepared by an ion-exchange between K^+ and Cd^{2+} ions followed by sulfurization with Na_2S. The H_2 evolution reaction under visible light irradiation of the catalyst was examined along with its structure.

Experimental

$K_4Nb_6O_{17}$ was prepared from Nb_2O_5 (Mitsui Kinzoku, 99.9%) and K_2CO_3 (Asahi Glass, Co. 99.5%) powders by melting at 1473 K for 15 min in a platinum crucible in air and then cooling down rapidly. This material was then crushed with a mortar to a fine powder of ca. 1—10 μm in diameter. The crystal structure was confirmed by X-ray diffraction (XRD). $Cd^{2+}/K_4Nb_6O_{17}$ was prepared by a cation exchange reaction between K^+ and Cd^{2+} as follows: 5 g of $K_4Nb_6O_{17}$ was stirred for 24 h in an aqueous $Cd(NO_3)_2$ solution (100 ml), then filtered and thoroughly washed with distilled water. The amount of Cd^{2+} ions substituted for K^+ ions in $K_4Nb_6O_{17}$ was controlled by the concentration of $Cd(NO_3)_2$ solution, and the degree of Cd^{2+} exchange was determined by X-ray fluorescence (XRF) measurements. The Cd^{2+}-exchanged sample, $Cd^{2+}/K_4Nb_6O_{17}$, was then sulfurized by Na_2S (0.5 M, 1 M=1 mol dm^{-3}) and washed with distilled water, followed by drying in air at room temperature. In this procedure, Na^+ ions are incorporated into the interlayer spaces with proceeding of Cd^{2+} sulfurization to compensate for the negative charge of niobate sheets. XRF measurements made us confirm that most K^+ ions which remained in $Cd^{2+}/K_4Nb_6O_{17}$ were substituted for by Na^+ ions via an ordinary ion-exchange process between K^+ and Na^+ ions. Although $Cd^{2+}/Na_4Nb_6O_{17}$ might more precisely express the present catalyst, the sulfurized catalyst will be referred to as $Cd^{2+}/K_4Nb_6O_{17}$ to lonk with the previous work.[12)] Ni loaded (0.1 wt% as NiO)–$K_4Nb_6O_{17}$ was prepared by impregnation of $K_4Nb_6O_{17}$ powder with aqueous $Ni(NO_3)_2$ solution. The catalyst was reduced by H_2 at 773 K for 2 h and was oxidized by O_2 at 473 K for 1 h. The structure of Ni loaded–$K_4Nb_6O_{17}$ was described elsewhere;[12,13)] ultra fine Ni metal particles (ca. 0.5 nm) are located at the interlayer I of $K_4Nb_6O_{17}$. Ni–$CdS/K_4Nb_6O_{17}$, was obtained from Ni–$K_4Nb_6O_{17}$ following the similar procedure of $CdS/K_4Nb_6O_{17}$ preparation. Neat CdS powder was prepared by addition of aqueous $Cd(NO_3)_2$ solution (0.5 M) to aqueous Na_2S solution (0.5 M) at room temperature. The mixture of the solution was stirred for 24 h. The resulting precipitation was filtered and then dried at room temperature.

Photocatalytic reactions were carried out in a closed gas circulation system equipped with a Pyrex reaction cell. Typically, 1 g of a catalyst was suspended by magnetic stirring in aqueous solution (300 ml) and was irradiated by a Xe lamp (500 W). A cut-off filter was inserted to remove the irradiation of wavelengths less than 420 nm. The amount of evolved H_2 was measured by gas chromatography (MS-5A column, Ar carrier) connected directly to the gas circulation system.

The catalyst was immersed in an aqueous H_2SO_4 solution (0.5 M, 100 ml) for 24 h at room temperature to remove CdS particles dispersed at the external surface of a $CdS/K_4Nb_6O_{17}$ catalyst. Under the same treatment, a neat CdS powder was completely dissolved within 1 h. After this treatment, X-ray photoelectron spectroscopy (XPS) showed that the peak intensity of Cd 3d had decreased to less than 10% of the non-treated one, and the color of the catalyst had turned from orange into light yellow.

Catalysts were characterized by XRD, UV-visible diffuse reflectance spectroscopy (UV-DRS), transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS). XRD, UV-DRS, and TEM measurements were carried out on instruments of Rigaku, JASCO UVIDEC 505, and JEM-2000FX (JEOL), respectively. EXAFS spectra were obtained by using the EXAFS apparatus at Beam Line 10B with synchrotron radiation emitted from the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF).

Results

Photoproduction of H_2 on Several $K_4Nb_6O_{17}$-Based Catalysts. Time courses of H_2 evolution under visible light irradiation on various catalysts in an aqueous K_2SO_3 solution (0.1 M) are shown in Fig. 2. Results of physically-mixed systems ($CdS+K_4Nb_6O_{17}$ and CdS+Ni–$K_4Nb_6O_{17}$) were previously reported.[12)] $K_4Nb_6O_{17}$ and Ni–$K_4Nb_6O_{17}$ themselves showed no activity because the band gap energy of $K_4Nb_6O_{17}$ (3.3 eV) was larger than the excitation energy ($\lambda>420$ nm). The rate of H_2 evolution on neat CdS powder was also very low (0.2 μmol h^{-1}). A noticeable enhancement of H_2 evolution rate (38 μmol h^{-1}) was observed for $CdS/K_4Nb_6O_{17}$ prepared via a cation exchange method, as shown in Fig. 2. This activity was about one order of magnitude higher than that of the physically-mixed system ($CdS+K_4Nb_6O_{17}$). Further increase of H_2 evolution rate to about twice was obtained on CdS/Ni–$K_4Nb_6O_{17}$ (71 μmol h^{-1}). The color change might be due to the reaction of CdS, as previously reported.[18,19)]

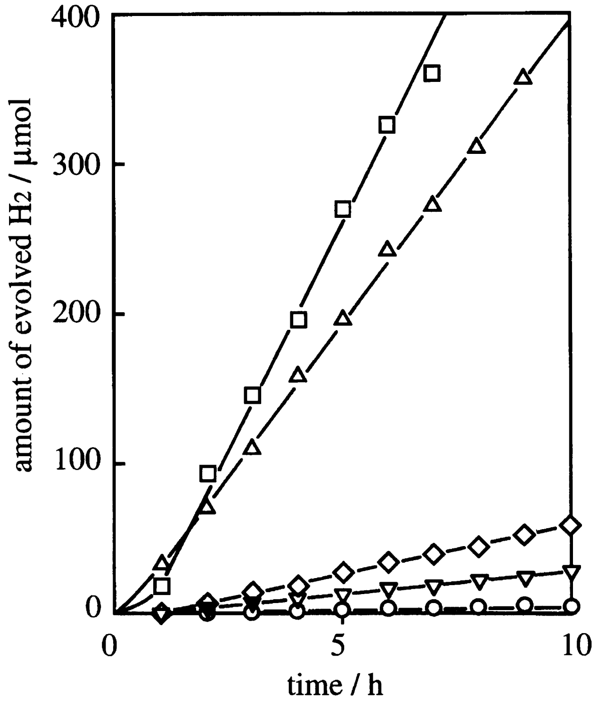

Fig. 2. Time course of H_2 evolution under visible light irradiation over various catalysts in aqueous K_2SO_3 solution; □: Ni–CdS/$K_4Nb_6O_{17}$, △: CdS/$K_4Nb_6O_{17}$, ◇: CdS+Ni–$K_4Nb_6O_{17}$, ▽: CdS+$K_4Nb_6O_{17}$, ○: CdS, solution (0.1 M, 300 ml) and Xe lamp (>420 nm).

Dependence of H_2 Evolution Rate on the Amount of Loaded CdS. Figure 3 shows the dependence of H_2 evolution rate upon the amount of CdS loaded on CdS/$K_4Nb_6O_{17}$ catalyst. The amount of loaded CdS was controlled by varying the degree of Cd^{2+} exchange as mentioned above. All catalysts were sulfurized at room temperature for one week. The rate of H_2 evolution increased with the amount of loaded CdS giving the highest activity at 3.2 wt% of CdS loading; the rate decreased when further CdS was loaded. The color of the catalyst remained yellow below 3.2 wt% of CdS loading during the photoreaction; however, it turned to dark yellow for the catalyst of 4.4 wt% of CdS loading.

The Effect of Sulfurization Condition on the Activity. H_2 evolution activity of CdS/$K_4Nb_6O_{17}$ varied markedly with the sulfurization condition. Figure 4 shows the effects of sulfurization temperature and time on H_2 evolution rate on CdS/$K_4Nb_6O_{17}$. The optimum condition was observed as in Fig. 4 when sulfurization was carried out at room temperature for one week. At 368 and 323 K, the activities reached the maximum values for 1 h and 1 d of sulfurization, respectively, and decreased for longer sulfurization periods. In case of sulfurization at 273 K, on the other hand, the activity still increased even after two weeks. During the sulfurization, the color of the catalyst changed from white to yellow with time; this occurred more rapidly at higher temperatures. For example, the color turned into deep yellow right after immersing the catalyst into Na_2S solution at 368 K, while at 273 K it stayed light yellow even after two weeks.

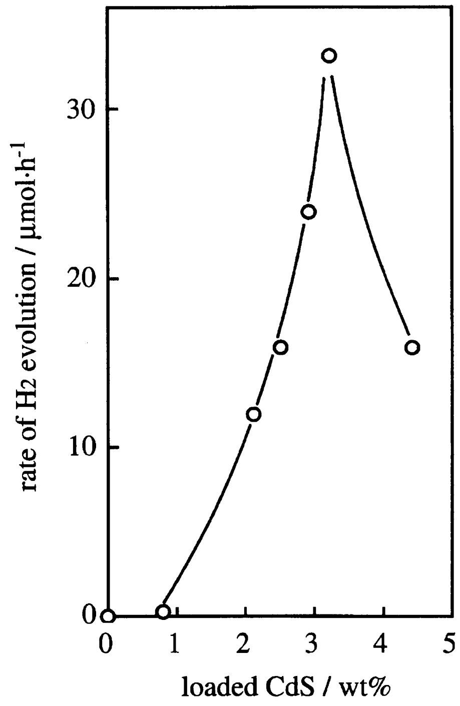

Fig. 3. Dependence of H_2 evolution rate over CdS/$K_4Nb_6O_{17}$ catalysts upon amount of loaded CdS in aqueous K_2SO_3 solution; solution (0.1 M, 300 ml) and Xe lamp (>420 nm).

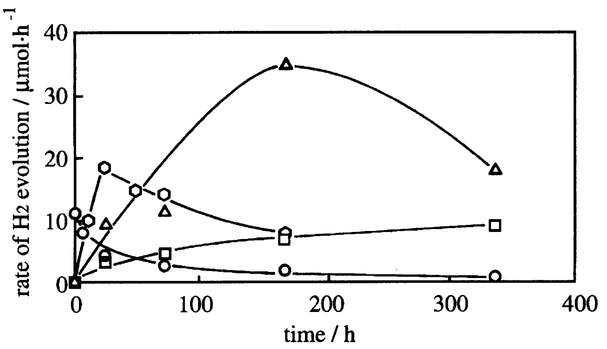

Fig. 4. Effect of sulfurization condition on H_2 evolution rate on CdS/$K_4Nb_6O_{17}$; △: sulfurized at room temperature, ○: 323 K, ○: 368 K, □: 273 K, solution (0.1 M, K_2SO_3 aq, 300 ml) and Xe lamp (>420 nm).

Change of H_2 Evolution Activity of CdS/$K_4Nb_6O_{17}$ by H_2SO_4 Treatment. As $K_4Nb_6O_{17}$ is a cation exchanger,[20,21] anions are not able to migrate into the interlayer spaces. It is, therefore, supposed that CdS particles at the interlayer spaces, if they exist, do not work efficiently for $SO_3{}^{2-}$ oxidation. $(C_2H_4OH)_3NH^+$, one of the cations which can intercalate into $K_4Nb_6O_{17}$,[20] was also used instead of $SO_3{}^{2-}$ as a sacrificial reductant for comparison.

$(C_2H_4OH)_3NH^+$ is expected to be oxidized more efficiently on CdS at the interlayer spaces. To examine this point, $CdS/K_4Nb_6O_{17}$ was treated by H_2SO_4 to remove CdS preferentially at the external surface of $K_4Nb_6O_{17}$. The amount of Cd remaining after H_2SO_4 treatment, as determined by XRF, was less than one third of that before the treatment.

In Fig. 5, the effects of H_2SO_4 treatment on H_2 evolution rate on $CdS/K_4Nb_6O_{17}$ in an aqueous K_2SO_3 and $(C_2H_4OH)_3NHCl$ solutions are compared. After H_2SO_4 treatment, the rate of H_2 evolution in an aqueous K_2SO_3 solution (0.1 M) markedly decreased from 38 to 0.06 $\mu mol\,h^{-1}$, and the color of the catalyst turned into dark gray after the reaction. The rate of H_2 evolution from $(C_2H_4OH)_3NH^+$ solution was 23 $\mu mol\,h^{-1}$ before the treatment and became 2.5 $\mu mol\,h^{-1}$ after the treatment. The relative activity of $(C_2H_4OH)_3NH^+$ compared with $SO_3{}^{2-}$ became rather high after the treatment although the absolute activity decreased by about one order of magnitude. Therefore, CdS is considered to remain at interlayer spaces as small particles.

XRD. The *b*-axis lengths of $K_4Nb_6O_{17}$ after various treatments were examined by XRD, as shown in Fig. 6. The main peak is attributed to (040) diffraction of $K_4Nb_6O_{17}$. No peak attributable to CdS was observed. The (040) peak of $Cd^{2+}/K_4Nb_6O_{17}$ at $2\theta=8.7°$ (b) decreased with sulfurization time, and a new peak at $2\theta=7.5°$ appeared, increasing in intensity ((c) and (d)).

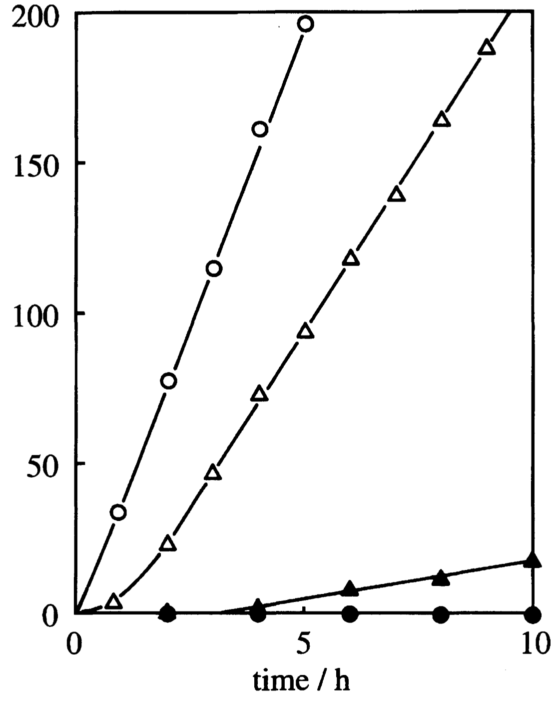

Fig. 5. Effect of H_2SO_4 treatment on H_2 evolution rate over $CdS/K_4Nb_6O_{17}$ in aqueous K_2SO_3 or $(C_2H_4OH)_3NHCl$ solution; K_2SO_4 aq ○: untreated, ●: treated, $(C_2H_4OH)_3NHCl$ △: untreated, ▲: treated, solution (0.1 M, 300 ml) and Xe lamp (>420 nm).

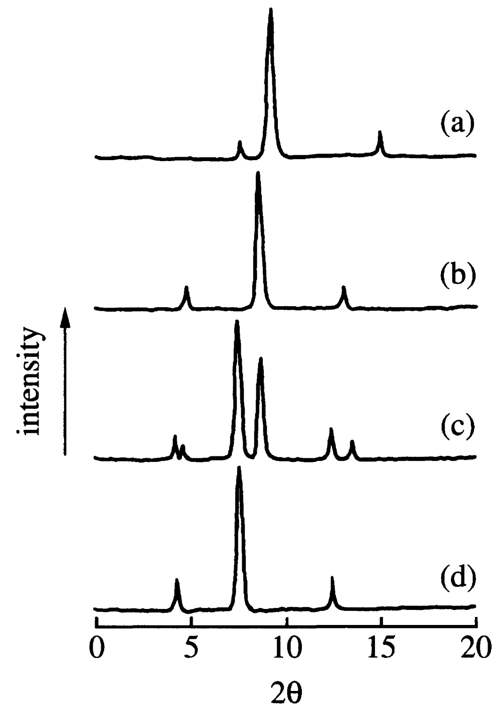

Fig. 6. XRD spectra of prepared catalysts; a) $K_4Nb_6O_{17}$, b) $Cd^{2+}/K_4Nb_6O_{17}$, c) $CdS/K_4Nb_6O_{17}$ sulfurized at room temperature for 24 h and d) $CdS/K_4Nb_6O_{17}$ sulfurized at room temperature for one week.

The *b*-axis length of $CdS/K_4Nb_6O_{17}$ was estimated to be 4.72 nm while it was 3.79 nm for $Cd^{2+}/K_4Nb_6O_{17}$. After sulfurization at room temperature for one week, the change of the interlayer space length completed. A similar but faster change of XRD pattern was observed for the samples sulfurized at higher temperatures.

EXAFS. Figure 7 shows the Fourier transforms of EXAFS functions $K^3X(K)$ for Cd K-edge absorption of various catalysts. The bond lengths and the average coordination numbers are summarized in Table 1. The peak at $R=0.216$ nm in an unsulfurized catalyst corresponds to the Cd–O bond. The peak at $R=0.252$ nm which appeared in sulfurized catalysts corresponds to the Cd–S bond of CdS. The sample sulfurized for one day showed both Cd–O and Cd–S bonds, while the lat-

Table 1. Cd K Edge EXAFS Data of $CdS/K_4Nb_6O_{17}$

Catalyst	Cd–O		Cd–S	
	R/Å	*N*	*R*/Å	*N*
$Cd^{2+}/K_4Nb_6O_{17}$ [a)]	2.16	5.5	—	—
$CdS/K_4Nb_6O_{17}$ [b)]	2.16	5.1	2.53	2.9
$CdS/K_4Nb_6O_{17}$ [c)]	—	—	2.52	3.6
CdS			2.52	4

R: interatomic distance between an absorber Cd atom and a scatter atom, *N*: average coordination number of the sphere, a) before sulfurization, b) sulfurized at room temperature for 24 h, c) sulfurized at room temperature for one week.

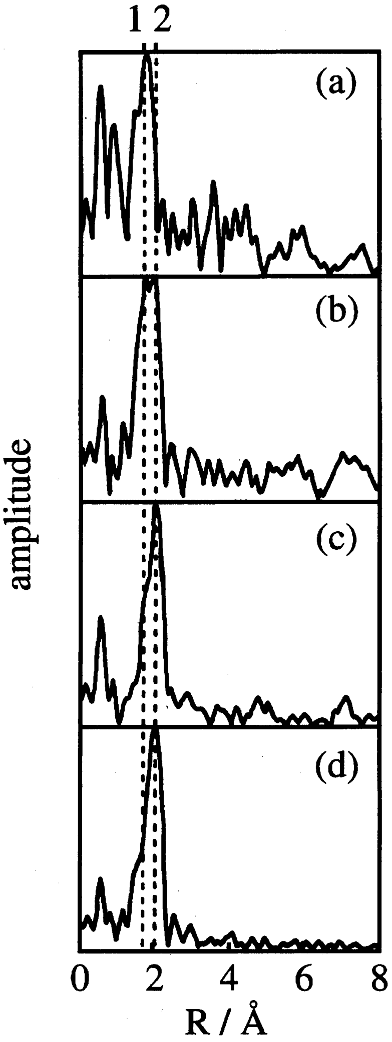

Fig. 7. Fourier transforms of Cd K edge EXAFS functions $K^3X(K)$ of $CdS/K_4Nb_6O_{17}$ catalysts and references; a) $CdS/K_4Nb_6O_{17}$, b) $CdS/K_4Nb_6O_{17}$ sulfurized at room temperature for 24 h, c) $CdS/K_4Nb_6O_{17}$ sulfurized at room temperature for one week and d) CdS. Interatomic distance 1 and 2 correspond to Cd–O bond in unsulfurized catalyst and to Cd–S bond in CdS prepared by sulfurization, respectively.

ter peak was dominant after sulfurization for one week.

TEM. One TEM photograph of $CdS/K_4Nb_6O_{17}$ is given in Fig. 8. Many CdS particles about 10 nm in diameter were observed at external surfaces of $K_4Nb_6O_{17}$ after sulfurization, while no CdS particle was observed after H_2SO_4 treatment.

UV-DRS. UV-DR spectra of $CdS/K_4Nb_6O_{17}$ before and after H_2SO_4 treatment, as well as that of neat CdS, are compared in Fig. 9. The absorption edge of the neat CdS was ca. 520 nm, it corresponded to the band gap energy of 2.4 eV. The absorption edge of $CdS/K_4Nb_6O_{17}$ was about 470 nm and that of H_2SO_4-treated catalyst was about 440 nm, which corresponded to the band gaps of 2.6 and 2.8 eV, respectively. These blue shifts may be attributed to the decrease of the particle size of CdS, i.e., so called size quantization effect.[22—25] By TEM, no CdS particles were observed at the external surfaces of H_2SO_4-treated catalyst, which indicates the existence of fine particles of CdS at the

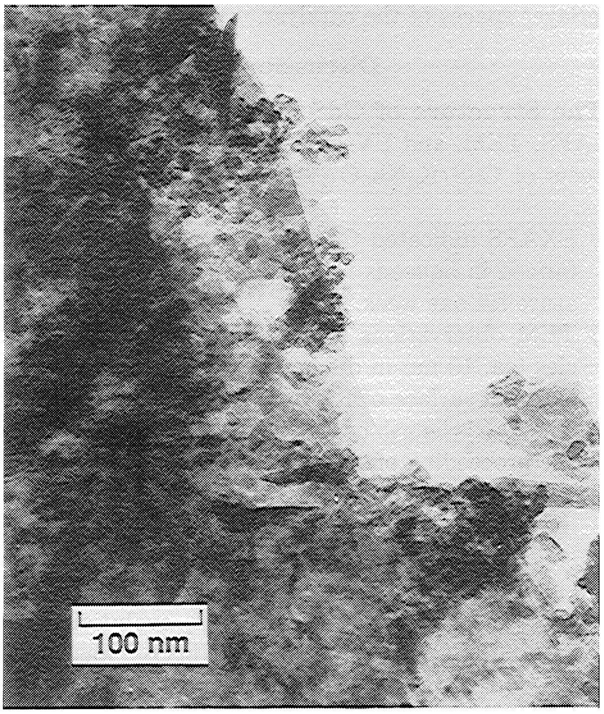

Fig. 8. TEM photograph of $CdS/K_4Nb_6O_{17}$ sulfurized at room temperature for one week measured by JEM-2000FX at 200 kV, ×270000

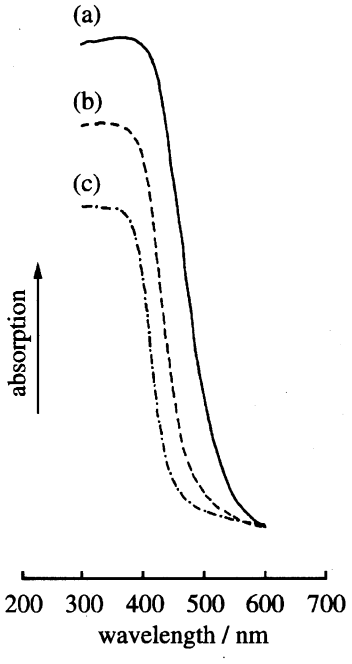

Fig. 9. UV-DR spectra of prepared catalysts; a) CdS, b) $CdS/K_4Nb_6O_{17}$ sulfurized at room temperature for one week and c) $CdS/K_4Nb_6O_{17}$ treated with H_2SO_4 after b).

interlayer spaces of the catalyst.

Discussion

The Structure of CdS/$K_4Nb_6O_{17}$. By XRD, EXAFS, TEM, and UV-DRS analysis, some structural aspects of CdS/$K_4Nb_6O_{17}$ have become clear, as follows:

(1) EXAFS indicated Cd^{2+} ions were completely sulfurized in aqueous Na_2S solution at room temperature for one week.
(2) TEM observations showed that many CdS particles (ca. 10 nm in diameter) were dispersed at the external surface of $K_4Nb_6O_{17}$ after sulfurization.
(3) The *b*-axis length of $K_4Nb_6O_{17}$ was expanded with the proceeding of sulfurization, as shown in Fig. 6.
(4) Although CdS particles at the external surface disappeared by H_2SO_4 treatment, the UV-DR spectrum indicated the existence of remaining small particles of CdS which were probably located at the interlayer spaces. H_2 evolution activity of H_2SO_4-treated CdS/$K_4Nb_6O_{17}$ was higher in $(C_2H_4OH)_3NH^+$ solution than in ${SO_3}^{2-}$ solution, in contrast to the result of untreated CdS/$K_4Nb_6O_{17}$. This difference also supports the existence of CdS at the interlayer spaces.

From these results, the structure of CdS/$K_4Nb_6O_{17}$ is schematically depicted as in Fig. 10(a).

The Mechanism of Sulfurization. A long sulfurization time, one week at room temperature, was required to obtain the optimum activity. Two different mechanisms are considered for sulfurization of Cd^{2+} ions in the catalyst.

(1) Cd^{2+} ions at first come out due to the ion-exchange reaction with Na^+ ions and then react with S^{2-} ions to form CdS particles outside the catalyst.
(2) H_2S (and HS^-, S^{2-}) migrates into the interlayer space, and sulfurizes Cd^{2+} ions there to produce CdS.

Ion-exchange between Cd^{2+} and Na^+ ions in Scheme (1) and intercalation of sulfur containing species in Scheme (2) may be the rate determining steps. Scheme (1) seems to be dominant in the present case, because most of CdS is considered to exist at the external surface, from TEM results and other observations.

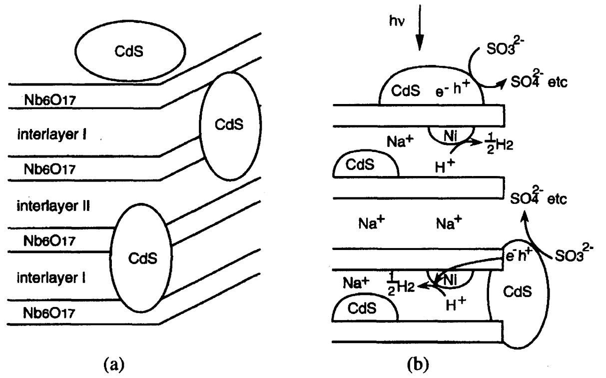

Fig. 10. A schematic structure of CdS/$K_4Nb_6O_{17}$ catalyst (a) and mechanism of H_2 evolution over Ni–CdS/$K_4Nb_6O_{17}$ from aqueous K_2SO_3 solution (b).

Electron Transfer from CdS to $K_4Nb_6O_{17}$. The results obtained in this study are reasonably explained by the electron transfer mechanism proposed previously:[17] Electrons are transferred from CB of CdS to that of $K_4Nb_6O_{17}$ and H^+ ions are reduced to H_2 on $K_4Nb_6O_{17}$. It was clearly demonstrated that CdS/$K_4Nb_6O_{17}$ showed a much higher activity than that of the mixture of CdS and $K_4Nb_6O_{17}$ particles. In CdS/$K_4Nb_6O_{17}$, as shown in TEM photographs, CdS particles (ca. 10 nm) are deposited over $K_4Nb_6O_{17}$, which must be favorable for the electron transfer. CdS at the interlayer spaces of the catalyst showed remarkably higher activity for H_2 evolution in $(C_2H_4OH)_3NH^+$ solution than in ${SO_3}^{2-}$ solution, even though the amount of CdS inside was much smaller than that outside. This may be explained by a more efficient electron transfer for intercalated CdS particles than that at the external surface. By the incorporation of ultra fine Ni metal particles at the interlayer spaces, the activity of H_2 evolution further increased. As shown in Fig. 10(b), this can be understood by considering that electrons in CdS are transported through the niobate sheets of $K_4Nb_6O_{17}$ to the Ni metal particles which are efficient catalytic sites for H_2 evolution.

Conclusion

CdS/$K_4Nb_6O_{17}$ prepared by a cation exchange reaction between K^+ and Cd^{2+} ions followed by sulfurization of Cd^{2+} with Na_2S showed much higher H_2 evolution activity than that of neat CdS or that of physical mixture of CdS and $K_4Nb_6O_{17}$ in K_2SO_3 solution under visible light irradiation ($\lambda > 420$ nm). This result is explained by the feasibility of H^+ reduction through electron transfer from CdS to $K_4Nb_6O_{17}$. The structural study of the catalyst revealed that most CdS particles existed at the external surface of $K_4Nb_6O_{17}$; a small amount of CdS was found as ultra fine particles at the interlayer spaces of $K_4Nb_6O_{17}$. It was also demonstrated that ${SO_3}^{2-}$ ions were oxidized by the CdS located at the external surface of the catalyst, while $(C_2H_4OH)_3NH^+$ ions were oxidized as well even by the CdS existing at the interlayer spaces, a difference is due to the cation exchange capability of the catalyst.

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