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Preparation of CdS : H-Beta Composites from Thiourea Complexes and Their IR Study

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Abstract — Zeolite–semiconductor composites (CdS particles distributed in H-Beta zeolite) were prepared and studied by IR spectroscopy and transmission electron microscopy. The composites were prepared by various procedures involving formation of the thiourea complex.
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Because of small size, nanosized semiconductor particles can be more active in photocatalysis than films and microparticles [1]. Microdispersed transition metal sulfides can be precursors of nanosemiconductors. Wang and Herron [2–4] demonstrated the principal possibility of constructing semiconductor particles (including nanoparticles) in zeolite pores by the example of CdS in sodalite pores. In further studies, other semiconductors and sodalites were examined [5]. As reported in [2], communicating CdS superclusters were obtained in zeolites of types X, Y, and A with pore sizes of 5 and 13 Å, and discrete $(CdS,O)_4$ cubes were detected. In that study, the composites were prepared by ion exchange of the zeolite with cadmium nitrate in aqueous solution, followed by treatment with H_2S; no CdS particles were detected by X-ray photoelectron spectroscopy on the zeolite surface even at high cadmium concentrations, which suggests formation of particles directly in the zeolite pores owing to ion exchange [2].

The use of thiourea complexes as semiconductor precursors is of interest, because the Cd–S bonds are already present in the complex, and these bonds and their surrounding are inherited by the pyrolysis product. Variation of the structure of thiourea complexes allows control of the structure of the resulting semiconductor materials. The goal of this study was to prepare zeolite–cadmium sulfide composites in H-Beta zeolite starting from thiourea complexes and to examine their formation process by IR spectroscopy.

Synthesis. As zeolite matrix we used H-beta zeolite (Si/Al = 12.5, SiO_2/Al_2O_3 = 25, Südchemie). Two different procedures were used to prepare zeolite–semiconductor composites.

(1) Adsorption by zeolite (Z) of the cadmium chloride thiourea complex $\{Cd[SC(NH_2)_2]_2Cl_2\}$ from aqueous solution, followed by pyrolysis of the adsorbed complex at 220°C with the formation of finely dispersed metal sulfide and gaseous products by reaction (1) [6, 7]:

$$\{Cd[SC(NH_2)_2]Cl_2\} \xrightarrow[\text{air}]{220^\circ C,} CdS + 2N_2 + 2HCl + H_2S + 2CO_2 + 2H_2O. \quad (1)$$

The pyrolysis can also yield intermediate products: thiocyanates, melam, and melem [7], which are subsequently oxidized to gaseous products [Eq. (1)]. Samples were tretaed in a 0.05 M solution of the complex for 24 h. We examined both thoroughly washed samples (i.e., containing only the adsorbed complex) and those without washing (i.e., containing excess complex on the surface).

(2) Solid-phase ion exchange between the zeolite and cadmium chloride (3.4 wt % Cd, according to [8]). The process [Eq. (2)] was performed in a muffle furnace:

$$2Z–O–H + CdCl_2 \xrightarrow{300–600^\circ, 24\ h} (Z–O)_2–Cd + 2HCl\uparrow, \quad (2)$$

where Z–O is zeolite.

Then the resulting zeolite sample was treated with a solution of thiourea; in so doing, the thiourea complex $\{(Z–O)_2–Cd–[SC(NH_2)_2]_2\}$ formed inside the zeolite. After that, the sample was thoroughly washed to remove excess thiourea and dried in an oven at

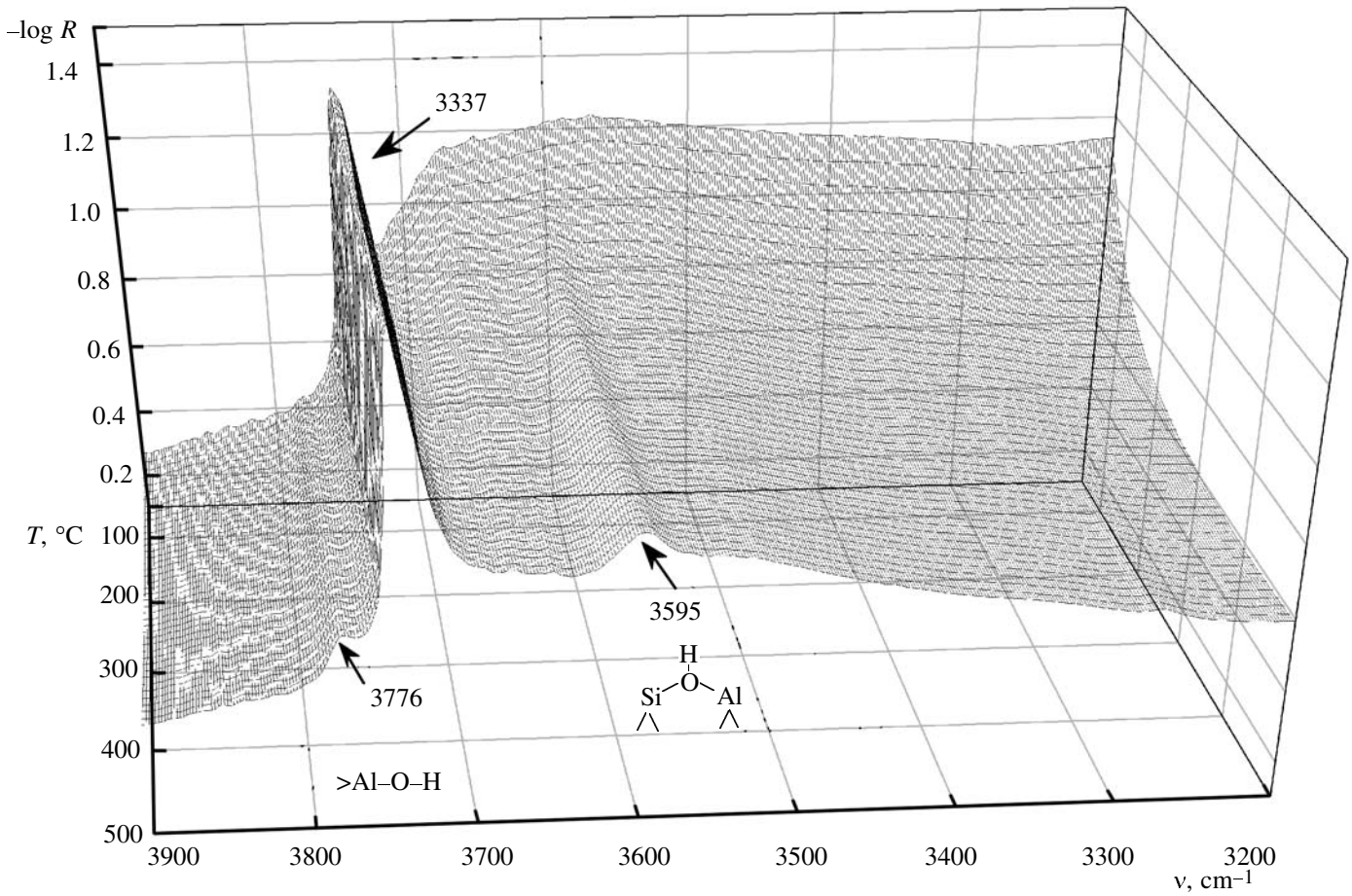

Fig. 1. DRIFT spectra of H-Beta in relation to temperature.

80°C. The subsequent heat treatment for 1 h at 220°C led to formation of the metal sulfide by reaction (3).

$$\{(Z\text{–}O)_2\text{–}Cd\text{–}[SC(NH_2)_2]_2\} \xrightarrow[\text{air}]{220^\circ C,} 2Z\text{–}OH + CdS + 2N_2\uparrow + CO_2\uparrow + H_2S\uparrow + 2H_2O. \quad (3)$$

IR spectroscopy. The solid-phase ion exchange and decomposition of the complexes were monitored by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy on a Bruker Equinox-55 Fourier IR spectrometer. Measurements were performed in a nitrogen flow in the range 500–8000 cm^{-1} at 50–500°C. The temperature was controlled with an HT MC1 programmable temperature regulator (Horst, Germany). Typically DRIFT measurements were performed at 500°C, because at this temperature the samples do not contain adsorbed water whose broad bands complicate interpretation of the spectrum. It is known that the reflected IR radiation is strongly influenced by the size of powder crystallites; therefore, all the spectra were normalized to the maximal intensity at 8000 cm^{-1}, where no sample-related absorption bands are observed. The spectra in this range are similar, and normalization allows semiquantitative comparison. Because of the wide range of wavenumbers, under the conditions of full light absorption, we chose the Olinger–Griffiths transformation [9] for data treatment:

$$A = -\log R_\infty,$$

where R is the reflection coefficient and A, optical density.

Transmission electron microscopy (TEM). TEM studies were performed on a Zeiss EM 902A device at 80 kV; resolution 1 nm. Samples were prepared for TEM as follows: A small amount of the composite (less than 50 mg) was ground in an agate mortar, 1 ml of hexane was added, and the mixture was stirred under ultrasonic treatment for 2–5 min. The resulting suspension was yellow. Then a drop of the solution

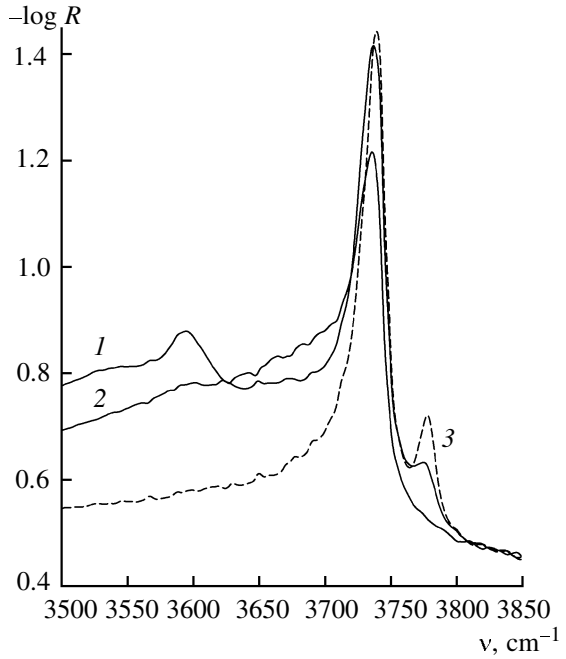

Fig. 2. FTIR spectra of H-Beta: (*1*) initial, (*2*) exchanged with $CdCl_2$ at 500°C, and (*3*) calcined at 600°C.

was applied onto a specially pretreated support for TEM with the applied graphite grid. The dried sample was used for TEM measurements.

Figure 1 shows the IR spectra of H-Beta zeolite recorded in the course of its heating to 500°C. Three bands belonging to isolated Al–OH (3760 cm^{-1}), interacting silanol (3745–3737 cm^{-1}), and bridging hydroxy groups (3600 cm^{-1}) [10] can be readily distinguished. At room temperature, a broad band at 3650–3200 cm^{-1} belonging to the O–H vibrations of water adsorbed in the zeolite and a band of silanol groups at 3745 cm^{-1} [11] are observed. As the sample is heated, the broad band disappears, i.e., water is desorbed, and the peak of silanol groups shifts to 3737 cm^{-1} and becomes narrower. This may be due to a decrease in the interaction of silanol groups with each other or with water.

It is known that the solid-phase ion exchange in the ZnO + H-ZSM-5 system occurs at temperatures exceeding 400°C [12]; therefore, in this study we annealed the $CdCl_2$ + H-Beta mixture at 500°C. The solid-phase ion exchange can involve various hydroxy groups (Fig. 2). Participation of a group in the ion exchange is accompanied by a decrease in the intensity of the corresponding band.

An IR study of the ion exchange of H-Beta with cadmium chloride shows that the bridging hydroxy group Si(OH)Al (3600 cm^{-1}) and the isolated framework group AlOH (3780 cm^{-1}) participate in the solid-phase ion exchange. The intensity of the band at 3600 cm^{-1} considerably decreases, and the band at 3780 cm^{-1} fully disappears (Fig. 2, spectrum *2*). Comparison of these spectra with the spectrum of H-Beta calcined at 600°C (Fig. 2, spectrum *3*) indicates that at this temperature the zeolite undergoes deformation: disappearance of bridging groups is accompanied by formation of an additional amount of terminal hydroxy groups AlOH. Thus, the optimal conditions for the ion exchange of H-Beta with cadmium chloride (3.4 wt % Cd) are 24 h at 500°C (muffle furnace).

Adsorption of thiourea and formation of the thiourea complex are accompanied by the appearance of strong bands at 1672, 3217, 3300, 3390, 3487 (Fig. 3, spectra *1–4*), 6467, and 6667 cm^{-1} and of a weak band at 4966 cm^{-1} in the DRIFT spectra. The samples heat-treated for 1 h at 220–250°C acquire a yellow color typical of cadmium sulfide. The formation of a cadmium complex with thiourea from the solution is confirmed by a shift of a strong C–S band at 738 cm^{-1} in the spectrum of free thiourea (TU) [13] to 727 cm^{-1} in the spectrum of $[Cd(TU)_2Cl_2]$, without significant changes in the band intensity. After the heat treatment at 220°C of the zeolite containing the adsorbed complex or the complex prepared by the reaction of the cadmium-ion-exchanged zeolite with thiourea, only a very weak band at 738 cm^{-1}, present also in the spectrum of the straight zeolite, is observed in the spectrum. This fact suggests decomposition of the thiourea complex at 220°C with the formation of CdS.

Since the free thiourea complex of cadmium melts at 210°C and completely decomposes at 250°C [14], the presence of the corresponding absorption bands shows that the zeolite framework exerts a stabilizing effect, i.e., the activation energy of the decomposition of the complex in the zeolite matrix is appreciably higher compared to the free complex. It is interesting that, upon longer heat treatment (24 h) at the same temperature, the samples lose color, which may be due to sublimation of fine CdS particles.

In the range of smaller wavenumbers, the bands of thiourea and thiourea complexes are obscured by absorption of the zeolite matrix (Fig. 4). However, we can note the absence of vibrations of free thiourea (738 cm^{-1}), confirming the formation of complexes with cadmium ions.

The pyrolysis of the complexes prepared in the zeolite by ion exchange with cadmium salts followed by treatment with thiourea results in reduction of bridging and terminal framework OH groups (Fig. 3, spectrum *4*). This fact confirms the formation of the complex inside the zeolite channels and occurrence of

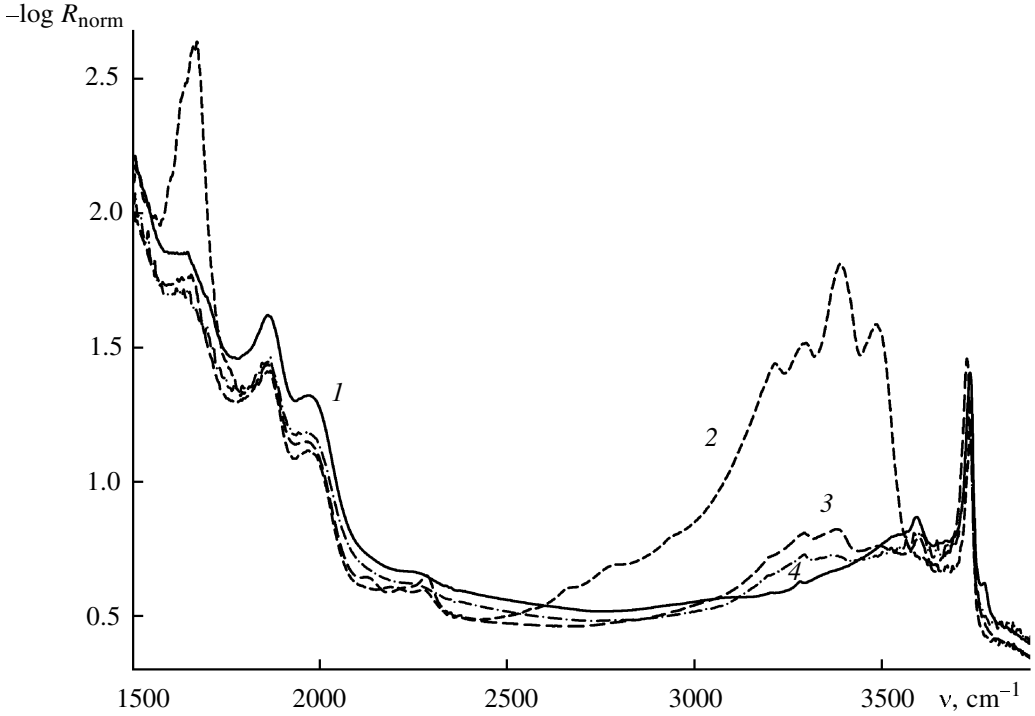

Fig. 3. FTIR spectra of H-Beta:CdS composites: (*1*) initial H-Beta, (*2*) H-Beta:CdS prepared with excess adsorbed complex, (*3*) H-Beta:CdS prepared by adsorption of the complex, and (*4*) H-Beta:CdS prepared by decomposition of the complex synthesized in the zeolite. Spectra measured at 500°C.

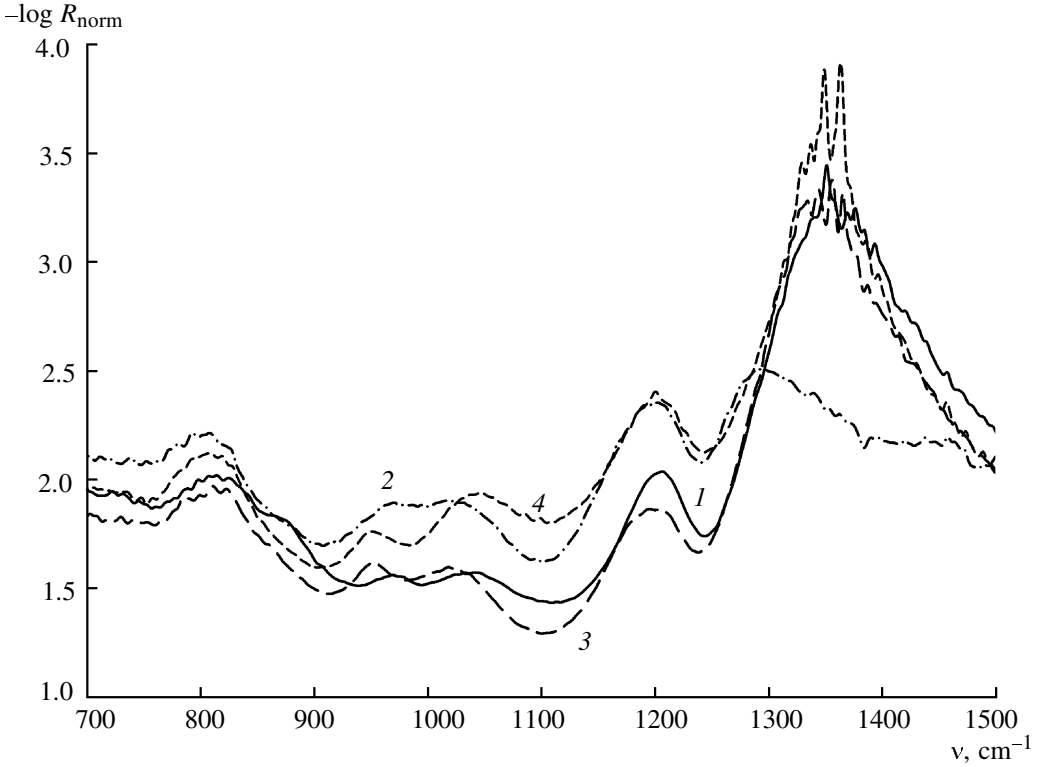

Fig. 4. FTIR spectra: (*1*) initial H-Beta, (*2*) H-Beta:CdS prepared with excess adsorbed complex, (*3*) H-Beta:CdS prepared by adsorption of the complex, and (*4*) H-Beta:CdS prepared by decomposition of the complex synthesized in the zeolite. Spectra measured at 500°C.

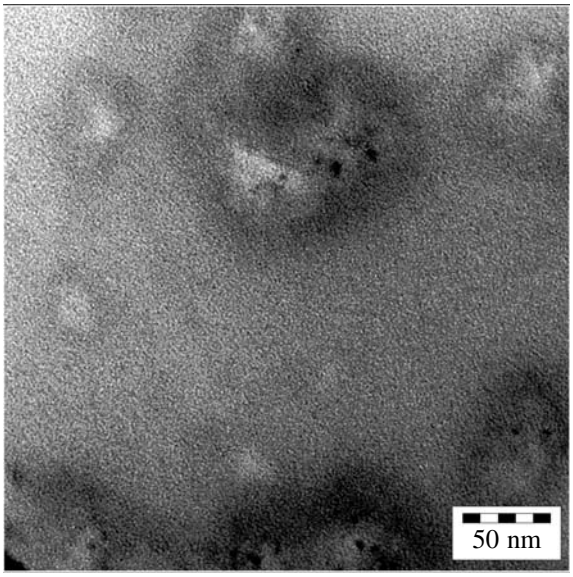

Fig. 5. TEM image of a composite sample prepared by synthesizing the cadmium thiourea complex in H-Beta zeolite.

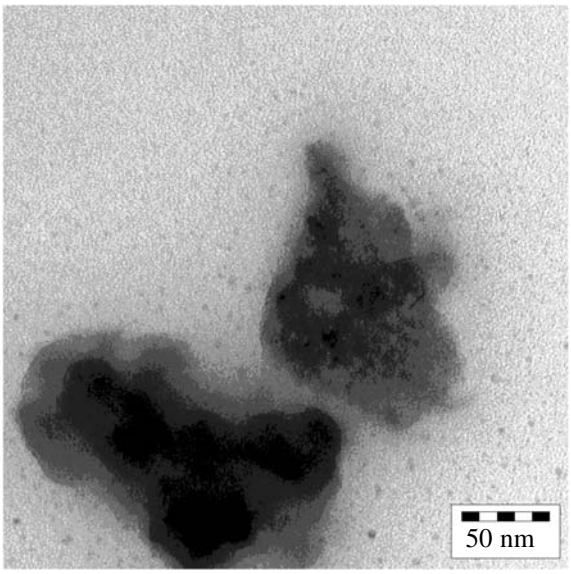

Fig. 6. TEM image of a composite sample prepared by adsorption of the cadmium thiourea complex in H-Beta zeolite.

reaction (3) and also suggests formation of CdS particles in zeolite pores.

The conclusions following from the IR data are fully confirmed by the TEM images. Figures 5 and 6 show the electron micrographs of the samples of H-Beta:CdS composites prepared by the synthesis of the cadmium thiourea complex inside the zeolite and by adsorption of the ready cadmium thiourea complex by the zeolite. According to published data, more or less dark coarse flakes in the figures are assigned to zeolite particles. In the TEM images of the samples prepared by the synthesis of the complex in the zeolite (Fig. 5), coarse sulfide particles are not observed against the background of the zeolite, but there are characteristic shadows near the zeolite particles, suggesting the presence of particles of size less than 1 nm in the zeolite. It is known that fine particles can be washed out from the support in the course of specimen preparation for TEM. This fact suggests that particles are formed inside zeolite pores, because the pore size is 5.5×5.5 and 7.6×6.4 Å [14].

It was also found that the adsorption of the ready cadmium thiourea complex in zeolite from solution, followed by pyrolysis, yielded metal sulfide particles of size 2–5 nm along with characteristic shadows assignable to particles of size smaller than 1 nm (Fig. 6). Taking into account the synthesis conditions and the zeolite pore size, we can assume that these particles are formed on the zeolite surface.

Thus, we prepared nanocomposites of cadmium sulfide in H-Beta zeolite from cadmium thiourea complexes and studied these nanocomposites by DRIFT and TEM.

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