

# Cyclodextrins Incorporated in Natural Zeolitic Materials of the Clinoptilolite Type

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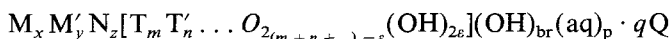
**Abstract.** Natural zeolitic material of the clinoptilolite type from a Czechoslovak deposit was found to be able to incorporate  $\beta$ -cyclodextrin. The new compounds, possibly of the host:guest type, were studied by thermal analysis, IR spectra and diffractographic measurements.

**Key words.**  $\beta$ -cyclodextrin, natural zeolitic material of the clinoptilolite type, host:guest compounds.

## 1. Introduction

New host and guest components are expanding the study and preparation of new compounds of this type [1–4]. Cyclodextrins ( $\alpha, \beta, \gamma$ ) are well known *hosts* in this context [5–8]. Cyclodextrins were described for the first time as the *guest* component by Kijima in 1984. They were enclosed in the natural mineral montmorillonite obtained from Japanese deposits and modified by Na(I), Ca(II) and Cu(II) ions [9, 10].

According to our results [1] cyclodextrins incorporated in natural Czechoslovak zeolitic material exhibit a similar phenomenon to those enclosed in montmorillonite. In our case the host component was a Czechoslovak zeolitic material of the clinoptilolite type. Its stoichiometry is given [11] by the general formula:



where  $\varepsilon = 0, 1, 2, 3 \dots$ , M and M' are exchangeable and non-exchangeable cations, species N are non-metallic cations (generally removable on heating), (aq) chemically bonded water (or other ligands), and Q sorbate molecules, which need not be water. Main group elements are among the T-atoms. In addition to Si and Al, Be, B, Ga, Ge, P and others can be used as T and T' atoms.

## 2. Experimental

### 2.1. MATERIALS

The natural zeolitic material of the clinoptilolite type (CT) from the East Slovakian deposit at Nižný Hrabovec was prepared by grinding to a grain size  $< 0.1$  mm.

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For its modification IM solutions of  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  (Lachema, Brno) were used.

The following cyclodextrins were used (CD):  $\beta$ -CD and hydroxypropyl  $\beta$ -CD (hpCD) from Chinoin, Budapest. For the modification of  $\beta$ -CD to the ethylenediamine form ( $\beta$ -CDen) we used: ethylenediamine (en), pyridine (b.p. 115°C, dried by distillation over BaO), 4-toluenesulphonylchloride (b.p. 67.5–68.5°C), purified by crystallization from a chloroform–petroleum ether mixture, all from Lachema, Brno.

## 2.2. METHODS

(1) In order to improve the sorptive abilities of the zeolitic material, this was partially modified by Ca(II) and Cu(II) ions. This was done by contacting with solutions of Ca(II) and Cu(II) salts (at room temperature) for a 10 day period [1, 2]. Then the product was washed with  $\text{H}_2\text{O}$ , centrifuged and dried in air for 48 h. This modification of the zeolite was analogous to the montmorillonite modification [9, 10].

(2)  $\beta$ -CD with bonded ethylenediamine (CDen) was prepared as follows: CDen was prepared according to [13] by the reaction of mono-6-*p*-toluene sulphonyl- $\beta$ -cyclodextrin (CDTs) with 1,2-diamino-ethane at 70°C in nitrogen. The isolation of the product was achieved by adding ethyl alcohol to the reaction medium.

(3) The preparation of the new host:guest type products was attempted in four ways by contacting for 10 days at 25°C 0.1 g of the appropriate zeolitic material and 8 mL of aqueous solutions (12.5 mM and 25 mM) of the CD [12]:

- (a) the clinoptilolitic zeolitic material (CT) with  $\beta$ -cyclodextrin ( $\beta$ -CD),
- (b) the clinoptilolitic zeolitic material (CT) in the Ca(II) and Cu(II) form (CTCa and CTCu) with  $\beta$ -CD,
- (c) the clinoptilolitic zeolitic material (CTCa or CTCu) with modified cyclodextrin CDen,
- (d) the clinoptilolitic zeolitic material (CTCa or CTCu) with hpCD.

Only methods (c) and (d) produced new compounds, the products being:

- (1) CTCa–CDen (using 12.5 mM CDen)
- (2a) CTCu–CDen (using 12.5 mM CDen)
- (2b) CTCu–CDen (using 25 mM CDen)
- (3) CTCa–hpCD (using 20 mM hpCD)
- (4) CTCu–hpCD (using 20 mM hpCD)

All products were centrifuged and dried in air for 48 h. Products (2a) and (2b) were identical.

The physical mixtures of starting materials were prepared by simple cogrinding in a mortar.

## 2.3. INSTRUMENTATION

Specord M 80 IR Spectrophotometer (Carl Zeiss Jena) in the 4000–200  $\text{cm}^{-1}$  range and using KBr discs (4 mg: 400 mg KBr). MOM 102 Derivatograph (Budapest) – TG 100 mg, DTA 1/5, DTG 1/5, heating rate 10°/min. Reference material  $\text{Al}_2\text{O}_3$ .

The diffractographic patterns were measured by the reflecting and transmission technique. In the former a standard Philips PW 1840 powder diffractometer with  $\text{CuK}_\alpha$  radiation and a Teflon sample holder was used, without internal standard.

In the latter a Guinier-Hägg focusing camera ( $r = 50.00$  mm) with monochromatic  $\text{CuK}_\alpha$  radiation, internal standard ( $\text{KCl}$ ,  $a = 6.2930$  Å) and photographic recording was used to obtain accurate data for further refinements. The film strips were measured with an automatic film scanner. At this stage no attempt was made to reproduce the film data with respect to intensities. For the CHN analysis a Perkin Elmer 2400 CHN Elemental Analyser was used.

For the morphologic study a Jeol Model JSM-35CF Electron Scanning Microscope was used.

### 3. Results and Discussion

#### 3.1. PREPARATION

During the preparation using methods (a) and (b) new products could not be prepared. However using ion exchanged zeolitic material new products were obtained with CDen and hpCD. The CHN analysis results are: *Found* for (1): C, 2.97; H, 1.47; N, 1.1; for (2): C, 2.28, H, 1.47; N, 0.96; for (3): C, 1.71; H, 1.28; N, 0.0; for (4): C, 1.31; H, 1.33; N, 0.0.

The results indicate the following cyclodextrin contents: 5.21% in (1); 4.0% in (2); 3.0% in (3) and 2.29% in (4).

#### 3.2. IR SPECTRA

Most of the characteristic bands of CDen and of the zeolitic material are also present in the IR spectra of the prepared products (Figures 1 and 2). The zeolitic

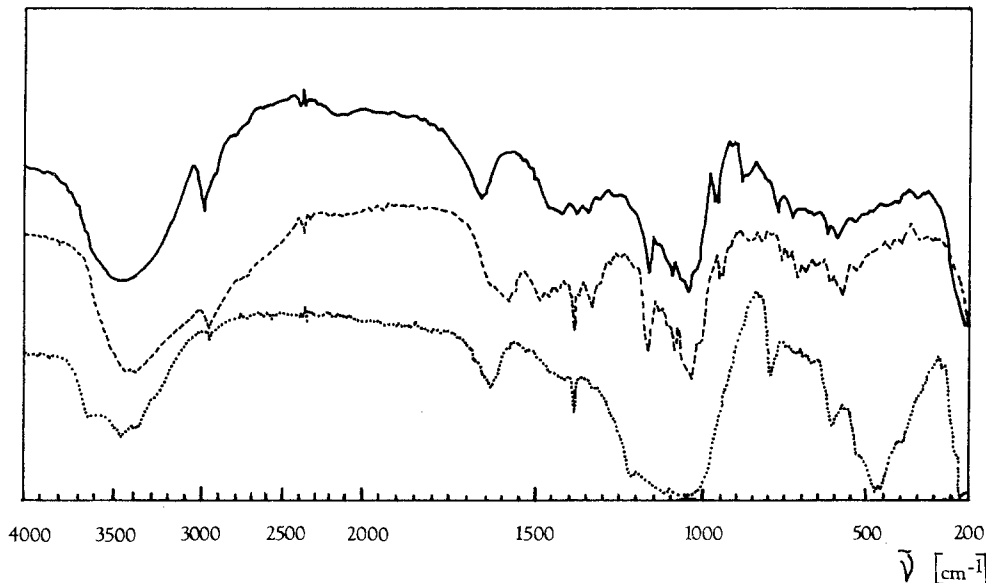


Fig. 1. IR Spectra of:  $\beta$ -cyclodextrin —; modified  $\beta$ -cyclodextrin: CDen - - -; the new product (2a) (CTCu-CDen) . . .

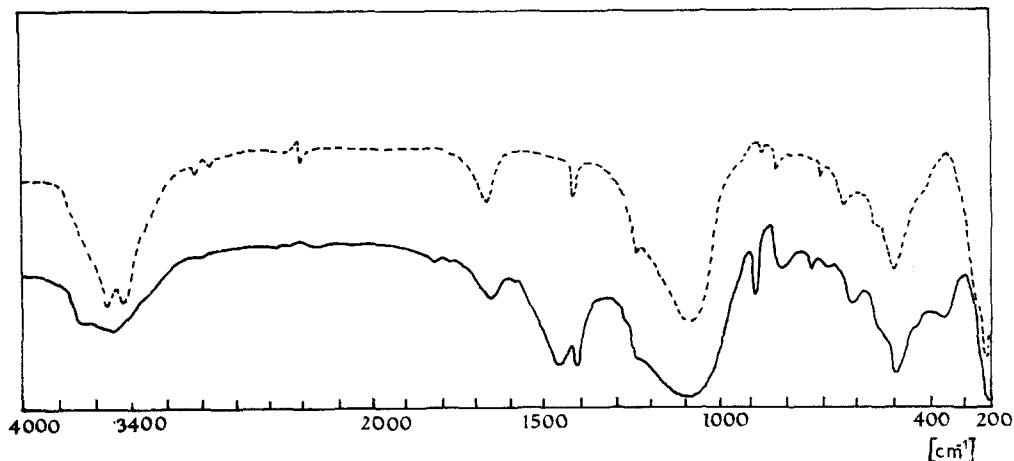


Fig. 2. IR Spectra: of the zeolitic material in Ca(II) form CTCa — the same in Cu(II) form CTCu ---.

spectral peaks ( $3640$ ,  $1635$ ,  $795\text{ cm}^{-1}$ ) were found with stronger intensities than those of the guest component. This could indicate [14] that the zeolitic material is the host in the new product.

In the IR Spectra of CDen (Figure 1) the band of  $\nu\text{CH}_2$  from en is observed at  $2944\text{ cm}^{-1}$ .

In the CTCu IR spectra the bands for  $\nu_{\text{as}}\text{OH}$  and  $\delta\text{HOH}$  at  $3370$ ,  $1630$ ,  $795\text{ cm}^{-1}$  (Figure 2) are present.

The IR spectra of the products prepared with hpCD (3), (4) again showed stronger intensities for the zeolitic spectral peaks.

The IR spectra of the products (Figure 1) show a broad band between  $1200$ – $800\text{ cm}^{-1}$  ( $\nu_{\text{as}}\text{Si}$ ,  $\text{Al—O}$ ) against the sharp band in the zeolitic material alone [17]. This broad band is ascribed in the literature [16] to the amorphous form of the East Slovakian zeolitic material. But the amorphous form was obtained only after heating.

### 3.3. THERMAL ANALYSIS

The results (Figure 3) show the following changes:

#### *Product CTCa–CDen (1)*

The decomposition starts at  $80^\circ\text{C}$ . It is interesting to observe that in spite of many distinct maxima on the DTA curve at  $295^\circ\text{C}$  (difference of  $20^\circ\text{C}$  against pure CDen),  $338$ ,  $558$ ,  $770$  and  $798^\circ\text{C}$  no strong decomposition of the organic compounds could be observed as in the case of CDen alone (Figure 3). But according to the TG curve this product was very slowly decomposed from  $80^\circ\text{C}$  to  $780^\circ\text{C}$ . The further step of the decomposition of the zeolitic material was not observed in our measurements.

The above thermal analysis, in comparison with that of the original CDen and with the clinoptilolitic zeolitic material in both forms, suggests that the CDen is incorporated into the clinoptilolite.

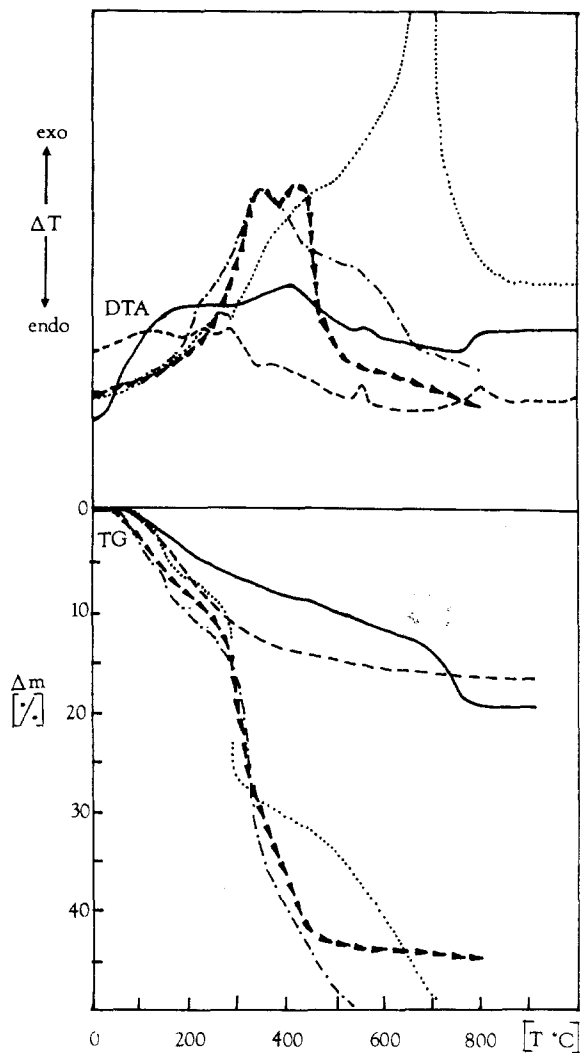


Fig. 3. DTA and TG curves of the products CTCa-CDen (1) — CTCu-CDen (2a) ---, CDen ... and of the physical mixtures CTCa + CDen - - - and CTCu + CDen ►►►.

#### Product CTCu-CDen (2a)

This compound showed very similar behaviour to the preceding product, with the decomposition starting at 80°C (Figure 3). There is no indication on the DTA curve of any strong decomposition of the organic compounds. There are however, many distinct partial decomposition steps, which are probably due to the coordination of the Cu(II) ions with the OH and H<sub>2</sub>O present in the clinoptilic material.

From the total loss of components during heating it seems that the product prepared from the Cu(II) form of the clinoptilic material is more stable than that prepared from the CA(II) form.

*Product CTCu-CDen (2b)*

This product was prepared using double the amount of CDen used for the preparation of **2a**. The IR spectrum of the product does not indicate a higher CDen content in the zeolite. This is a confirmation, that the amount of sorbed CDen depends on the steric properties of the host framework.

*Product CTCa-hpCD (3)*

This compound starts its decomposition at 42°C (Figure 4) and loses about 16% of its weight by 900°C. This differs from the original hpCD and the zeolitic material

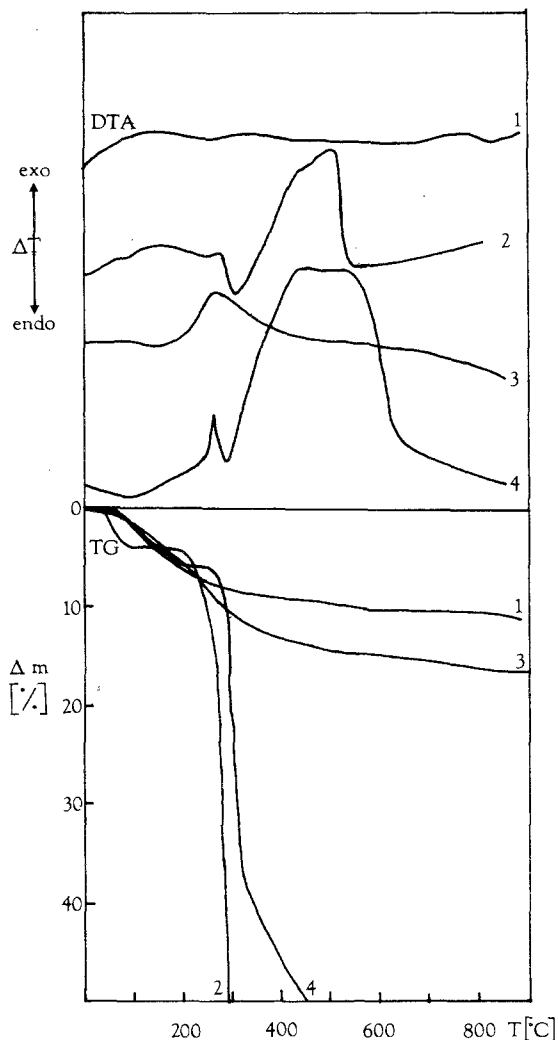


Fig. 4. DTA and TG curves of the product CTCa-hpCD (3), starting materials CTCa (1) hpCD (2), and of their physical mixture (4).

indicating the possible enclosure of the hpCD and the stabilisation of the product (3) as compared with hpCD alone.

#### Product CTCu-hpCD (4)

This compound again starts its decomposition at 42°C (Figure 5) and loses only about 15.5% by 900°C. The DTA and TG curves of this product again differ markedly from those of the starting materials.

We may observe on the DTA curve of all five products many endothermic and exothermic processes but these seem to be masked in one process of the decomposition according to the TG curve.

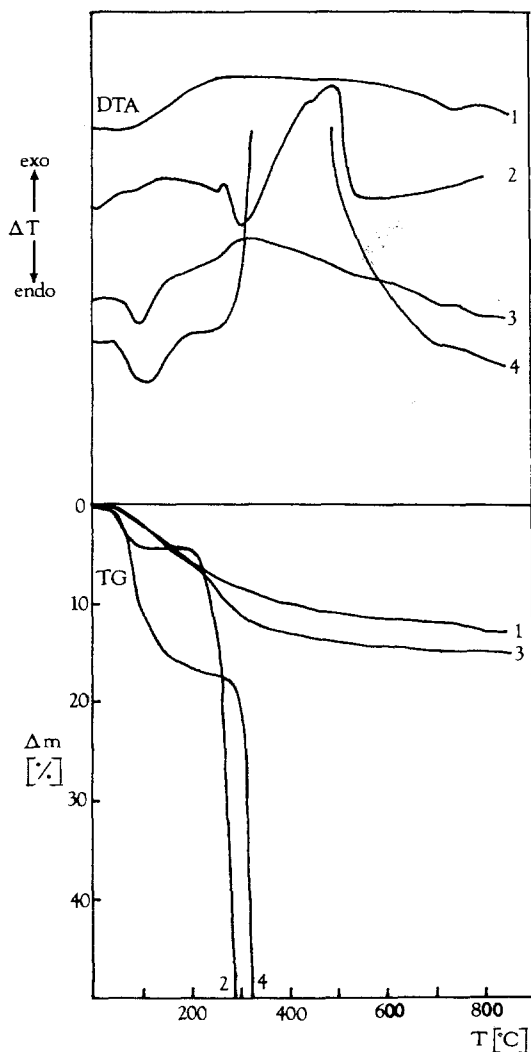


Fig. 5. DTA and TG curves of the product CTCu-hpCD (3), starting materials CTCu (1) hpCD (2), and of their physical mixture (4).

The outer diameter of  $\beta$ -cyclodextrin is about 1.53 nm. The Czechoslovak natural zeolite of the clinoptilolite type used here has according to Pechár [16] the following parameters:  $a = 0.7046$  nm,  $b = 1.7908$  nm,  $c = 1.1613$  nm,  $\beta = 90.58^\circ$ . Alberti has determined other parameters and a different angle [16] for clinoptilolite (heulandite type) samples from two different foreign deposits. The pore sizes were determined to be  $0.76 \times 0.3$  nm and  $0.46 \times 0.33$  nm. Until the structure of the Czechoslovak clinoptilolite sample used in our work can be solved more precisely, we may only suppose that these facts enable some kind of incorporation of the cyclodextrin guest.

But the physical mixtures of all the starting cyclodextrins and the zeolitic materials (Figures 3, 4 and 5) show strongly different features of their decomposition. The differences are to be seen on the DTA and TG curves. This is considered to be the most important indication of the enclosure of CD in the products (1)–(4).

According to the thermal analysis the weight loss due to guest water in the zeolitic material is 13.3% in agreement with [16]. The results of TA of the zeolite and of the products agree with the chemical analysis in a satisfactory way for products (4), (3), (2) and (1).

Comparison of the results of CHN analysis and the weight loss on the TG curve ( $\Delta m$  product –  $\Delta m$  zeolitic material) gives the following data about the incorporated quantity of cyclodextrins:

Compound	Amount of G	
	$\Delta$ mass [%]	G [%]
(1)	6,7 (20 – 13,3)%	5,21%
(2)	3,7 (17 – 13,3)%	4,0 %
(3)	2,7 (16 – 13,3)%	3,0 %
(4)	2,2 (15,5 – 13,3)%	2,29%

#### 3.4. DIFFRACTOGRAPHIC MEASUREMENTS

Diffraction measurements of the newly prepared compounds suggest that an amorphous form was created in all four cases which is a consequence of the decomposition and substitution of the  $H_2O$  present as the original guest in the zeolite. During the desorption of the water molecules from the zeolites the change of the crystalline structure to the amorphous form [13] is common. This phenomenon is clearly observed in the case of these products not only in the diffraction measurements (Figure 6), but also in their IR spectra.

The characteristic diffraction data obtained by the reflecting technique for pure  $\beta$ -CD,  $\beta$ -CDen, the natural zeolite, the empty sample holder (Teflon) and the three zeolite preparations (first activated with Ca and Cu salts) and their products with CDen (of different concentrations) showed that diagrams of the last three samples are identical to each other and also to the untreated mineral.

The ternary system: mineral, guest components (cyclodextrins and salts) can be looked upon as dispersed systems. The dispersed mineral phase is completely



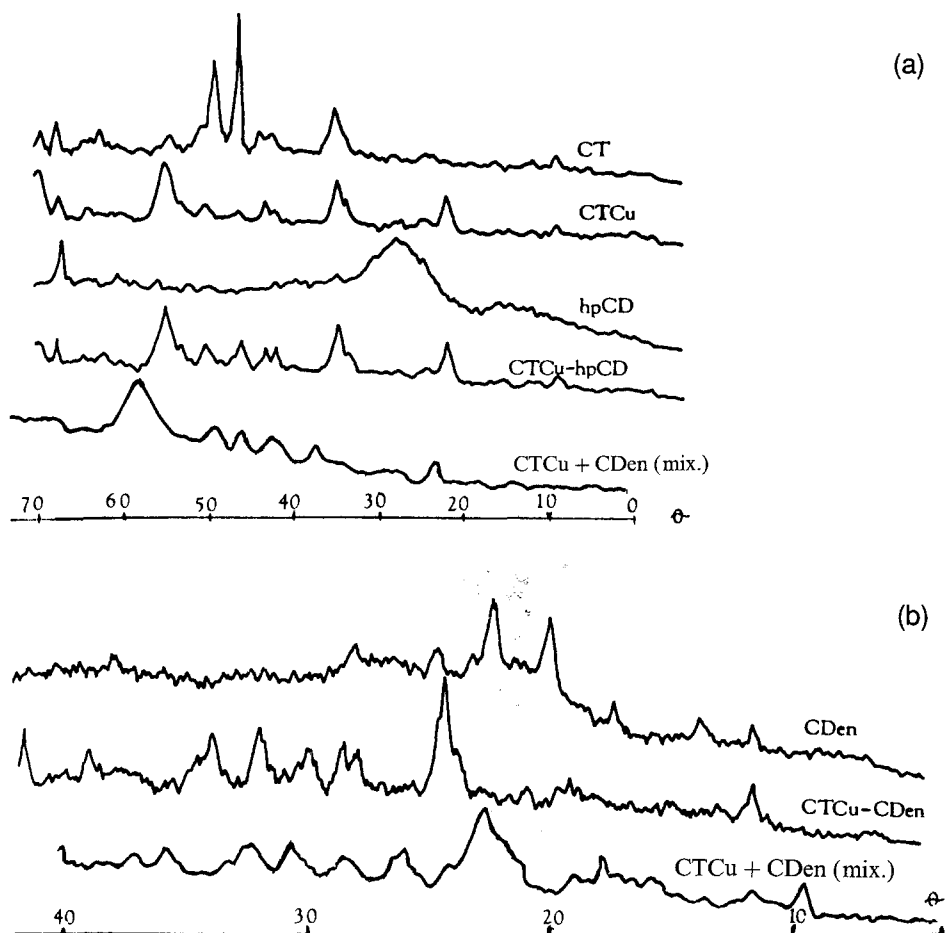


Fig. 6. Diffractographic pattern of the starting materials, products and physical mixtures: (a) CT, CTCu, hpCD, CTCu-hpCD, CTCu + hpCD (mixture); (b) CDen, CTCu-CDen, CTCu + CDen (mixture).

undisturbed by the different suspended media and the latter cannot be detected by X-ray methods due to the distribution of the guest component molecules throughout the dispersed zeolite phase. In this way the guest materials occur with short range order too short to be detected by X-ray wavelengths. However by using electron diffraction techniques it may be possible to register the characteristics and identify such samples.

The physical mixtures prepared by cogrinding of the starting materials differ slightly in all cases from our products. According to other authors in the case of low content of the guest the physical mixtures never exhibit strong decisive XRD signals.

### 3.5. ELECTRON MICROSCOPIC PATTERNS

Electron microscopic pictures of the starting materials and of the product (2) using the same magnification are compared in Figure 7.

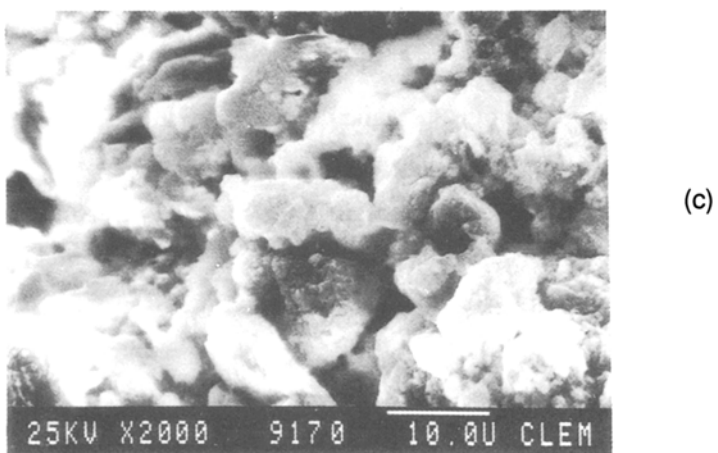
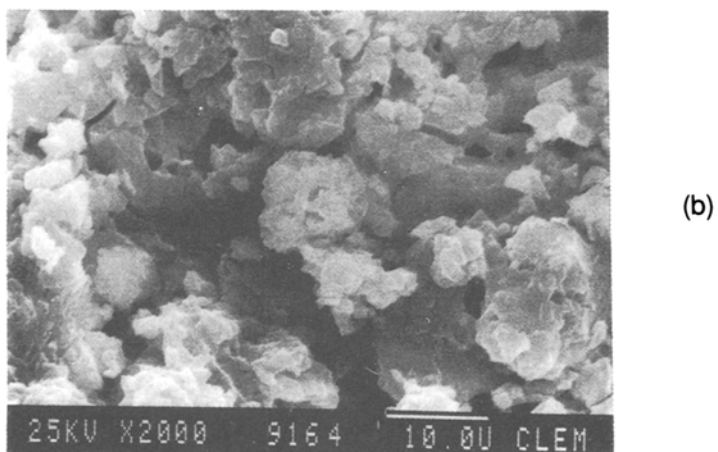
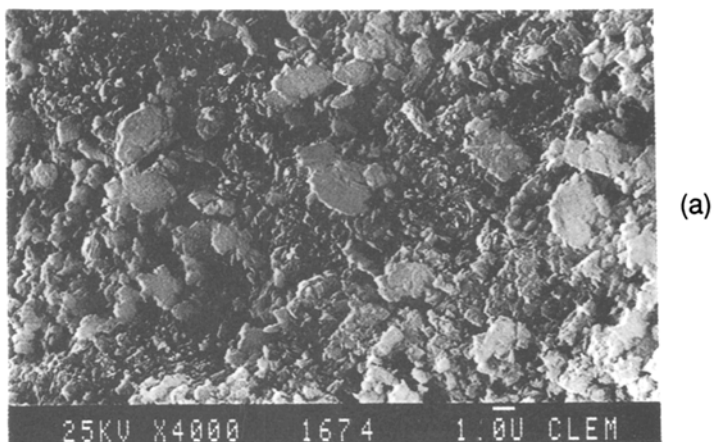


Fig. 7. Electron microscopic picture of the starting materials (a) CT; (b) CDen and (c) of the product (2).

#### 4. Conclusions

New products have been formed. The thermal stability of the clinoptilolitic zeolitic material is conserved in the products. Both components of the products – the zeolitic material and cyclodextrins – are harmless from the physiological view point. In fact both are used, the cyclodextrins in the pharmaceutical and food industries and the zeolitic materials in agrochemistry. After the inclusion of a guest compound into the CD and then by the further preparation into the zeolitic material, the release temperature of such compounds or of the cyclodextrins could be increased in an extraordinary way.

These properties suggest that compounds of this type could be used for the encapsulation of compounds into the zeolites and as sorptive materials in high temperature gas chromatography.

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