MODIFICATION OF CLINOPTILOLITE BY SYNTHETIC ZEOLITE

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The sol–gel process allows to modify clinoptilolite by the nucleation of synthetic zeolite. From the viewpoint of methanol conversion, the obtained high Al content nucleation-deposited zeolite decreases the catalytic activity of clinoptilolite. Therefore, it is necessary to optimize the selection of suitable synthetic zeolite as to its composition. Contamination of zeolite surfaces by carbonaceous fragments during catalytic process results from physico-chemical characteristics of the used and processed zeolite, and according to DTA and TG analysis it significantly affects the readsorption of water vapours and likely also the zeolite activity in methanol conversion.

It is well known that both synthetic and natural zeolites have found the widespread use in catalysis of chemical processes. Catalytic characteristics of zeolites have been modified by changing the Si/Al ratio, mostly by extraction of Al from the zeolite lattice using acetylacetone, phosgene, $Cl_2(g)$ or, on the other hand, by alumination of zeolite with vapours of selected aluminium compounds[1,2] ($AlCl_3$, $AlBr_3$).

The Si/Al ratio has a significant influence on the internal structure and on the position of OH groups. Therefore, the acidity of the respective zeolite, which is the principal characteristics affecting the catalytic activity of zeolites[3], is also affected.

In our study we made an attempt to modify the above properties by depositing or nucleation of a synthetic zeolite on the natural zeolite – clinoptilolite (Nižný Hrabovec, The Slovak Republic) – for methanol conversion, for which the catalytic activities of the natural, modified and extracted (2,4-pentanedione) forms of zeolite have been tested.

EXPERIMENTAL

Ground clinoptilolite of the grain size <40 μm was used as a starting material. Modification was carried out by sol–gel process in a flask provided with a reflux condenser at the boiling point of a suspension consisting of 15 g of clinoptilolite, 1.5 g NaOH (p.a.), 1 g $NaAlO_2$, 0.8 g Na_2SiO_3 and 60 ml H_2O. Sodium aluminate and sodium silicate were obtained by remelting of the respective oxides with NaOH followed by their subsequent dissolution in distilled water.

The zeolite modified in this way (MZ) was washed with distilled water and dried at 105 °C/1 h. The sample MZ and the parent clinoptilolite were activated after the preceding ion exchange with $(NH_4)_2SO_4$, by heating[4] at 550 °C/3 h.

Methanol conversion was carried out in a temperature-controlled tube reactor (U-tube), 1 cm in diameter, on the zeolite deposited on the bed of glass beads. A total of 1 g of zeolite was used, total time of the reaction was[5] 30 min at the temperature 375 °C and LHSV = 25. Reaction products were analyzed by gas chromatography (TCD, CHROM 4).

Volumetric analysis of clinoptilolite and the degree of ion exchange were obtained by AAS. Electron microscopy was used to examine the surface morphology. Al was extracted from both zeolite forms (clinoptilolite and MZ) with 20% solution of acetylacetone in benzene under reflux at constant stirring during 3 h. The Al content was determined by a semiquantitative EDX (energy dispersion X-ray) microanalysis. Total zeolitic surfaces were measured volumetrically by N_2 adsorption at −196 °C.

The acidity and changes of zeolite samples due to processing were determined by IR spectroscopy (SPECORD M80) – KBr technique of analysis of solids, where the KBr : zeolite ratio was 400 : 1 and the pressure 30 MPa . DTA and TG analysis were carried out using a derivatograph Q-1500D (MOM).

Total amount of the carbon deposited during the reaction on zeolites was determined volumetrically[6], by combustion to CO_2.

RESULTS AND DISCUSSION

Morphology of the surface of clinoptilolite and MZ is shown in Figs 1*a*, 1*b*. Figure 1*a* illustrates the relief surface of a zeolite particle ≅ 30 μm before the sol–gel modification process. One can observe a visible nucleation – i.e. deposited particles of the synthetic zeolite of average particle size ≅ 2 μm, moderate in the surface relief, on the surface of the processed zeolite (Fig. 1*b*).

Chemical composition of the natural zeolite and the nucleation-deposited particles of the synthetic zeolite can be compared based on data in Table I which summarizes the results of EDX microanalysis of clinoptilolite and of the spherical MZ particles. The results of the volumetric analysis of clinoptilolite obtained by AAS are presented in Table II. This table shows also the percentage of the ion exchange of Na, K, Ca for the NH_4^+ of the clinoptilolite sample, displaying the highest exchange degree reached for K

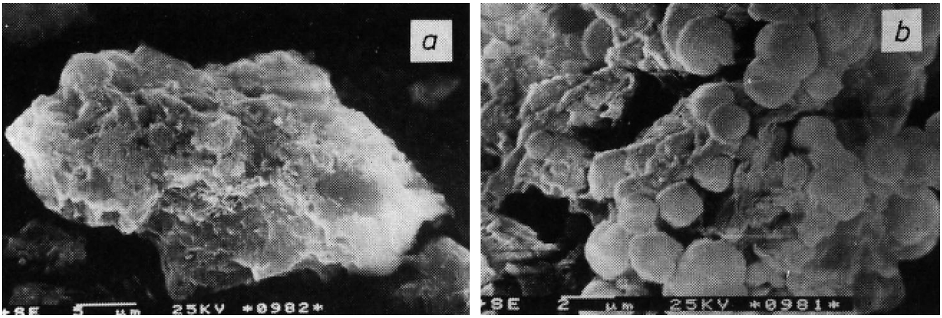

FIG. 1

Surface morphology of clinoptilolite (*a*) and MZ (*b*) and Ca. The total Al contents determined by AAS method in clinoptilolite and MZ are 5.47 wt.% and 6.5 wt.%, respectively.

The total surface determined by N_2 adsorption was 29.1 m^2/g and for MZ 26.9 m^2/g. It follows that the nucleation of the synthetic zeolite on clinoptilolite smooths out the clinoptilolite surface, and at the same time it decreases the total surfaces, in spite of its anticipated partial increase caused by formation of spherical particles. The possible fine nucleation taking place in the inner zeolitic space cannot be excluded.

DTA and TG analyses of the natural and activated forms of clinoptilolite and of the activated form of MZ are presented in Fig. 2. Natural clinoptilolite as well as two other forms show a pronounced endo effect at 105 °C, associated with the elimination of the physically adsorbed water. The weight of the natural clinoptilolite decreases continuously with temperature up to 690 °C when zeolite dehydroxylation occurs with the endo effect at 705 °C. The weight loss up to 690 °C amounts to 12.7 wt.% and at the dehydroxylation to 1.1 wt.%. Dehydroxylation of the activated form of clinoptilolite

TABLE I
EDX microanalysis of clinoptilolite and of spherical MZ particles

Zeolite	Content, wt.%						Si/Al molar ratio
	Na	Al	Si	K	Ca	Fe	
Clinopt.	2.32	16.64	69.92	3.17	1.54	6.41	4.20
MZ	17.17	32.10	50.73	–	–	–	1.52

TABLE II
Average content of selected elements of clinoptilolite (AAS) and the extent of ion exchange

Element	Content, wt.%	Ion exchange, %
K	0.52	98.0
Na	0.14	25.2
Ca	1.68	72.0
Mn	0.02	–
Al	5.47	–
Si	38.20	–
Fe	0.95	–

with an insignificant endo effect at 735 °C begins at 690 °C with the total weight loss 1.1 wt.%. The loss of physically adsorbed water amounted to 9.3 wt.%. Dehydroxylation of the activated MZ occurs at 585 °C, with the weight loss 1.2 wt.%, however, without a measurable endo effect. The content of the physically adsorbed water was 10.6 wt.%. Dehydroxylation of the activated MZ begins at the lower temperatures, which suggests the existence of weaker OH group bonds. It proceeds without a significant endo effect.

Comparison of the IR spectra (Fig. 3) indicates that the nucleation resulted in the shift of the band maximum of clinoptilolite from 1 085 cm^{-1} to 1 040 cm^{-1}, and the spectrum in the region below 800 cm^{-1} contained additional peaks to those observed at 800, 620, and 480 cm^{-1}. Details in Fig. 3 show the positions of OH groups and allow to discern three types of OH groups, i.e. bands at 3 745, 3 780, and 3 640 cm^{-1} for clinoptilolite and at 3 725, 3 745, 3 780, and 3 635 cm^{-1} for MZ. The high frequency bands above 3 700 cm^{-1} correspond to the valence vibrations of the OH groups not hydrogen-

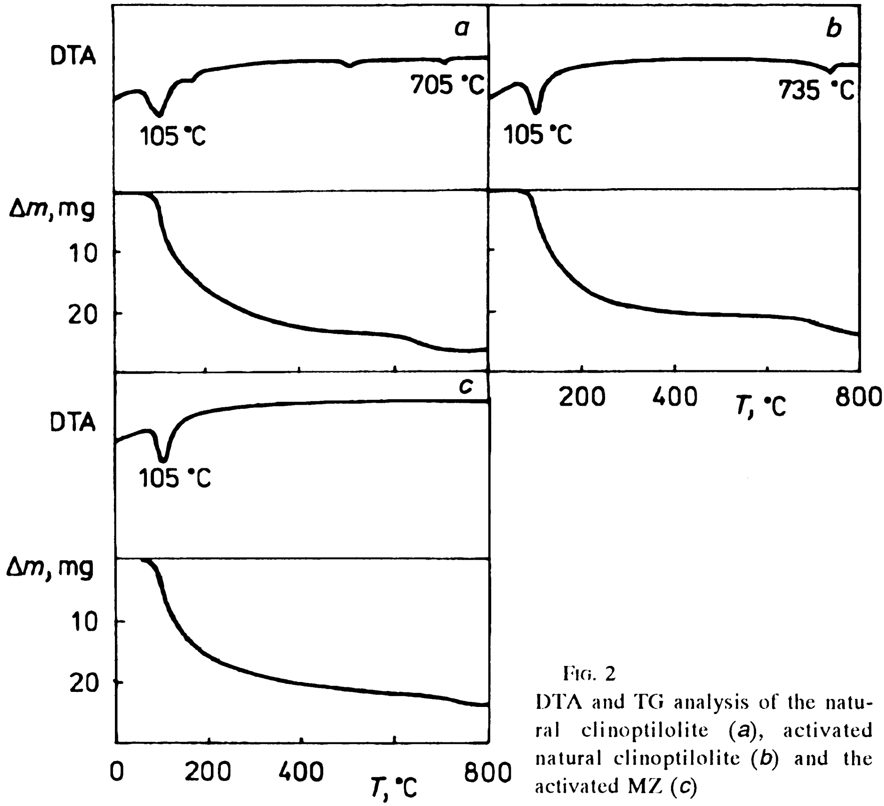

FIG. 2
DTA and TG analysis of the natural clinoptilolite (*a*), activated natural clinoptilolite (*b*) and the activated MZ (*c*)

bonded which are present in lattice defects[3,7]. The bands at 3 640 and 3 635 cm^{-1} correspond to the hydrogen-bonded OH groups or they represent the bridging hydroxyls. A slight shift by 5 cm^{-1} of the band at 3 640 cm^{-1} to 3 635 cm^{-1} for MZ also points to the existence of somewhat more acidic OH groups.

Data for methanol conversion at 375 °C at the beginning of the reaction and after 30 min are shown in Table III. The degree of methanol conversion on the activated clinoptilolite was 94.9% and on the activated MZ 79.9%. Figure 4 shows time dependences of the degree of conversion on all the forms of clinoptilolite used in the present study. On the activated clinoptilolite and MZ a slight initial decrease of the activity which is observed to approx. 5 min from the beginning of the reaction is likely caused by the coverage of the surface active sites of the catalyst by carbonaceous fragments. In the initial time interval from 5 to 15 min, the zones practically without changed conversion degree are observed, and only after that time, a sudden decrease of the conversion takes place due to a depreciation of the active sites in the internal cavities of the zeolites. In the case of the extracted forms of clinoptilolite, the zone with the unchanged degree of conversion (plateau) is not observed, and the decrease of the activity takes place continuously during the catalytic reaction. This is apparently connected with the change of dimensions of internal cavities, and thus consequently with the change of the diffusion rate of the compounds formed into the interior of zeolite cavities. The activated clinoptilolite and the activated MZ contained 4.6 wt.% and 2.9 wt.% C, respectively. Due to our experimental arrangement and LHSV, aromatic substances[5] were not produced, and dimethyl ether (DME) was obtained as the dominant component.

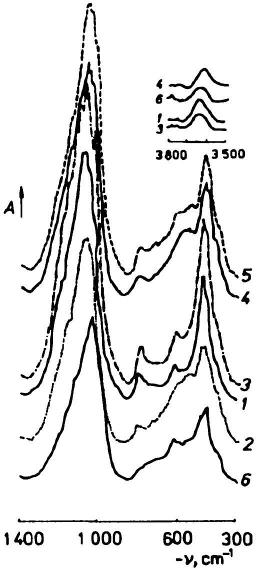

FIG. 3

Comparison of IR spectra of the extracted (*1*), extracted after reaction (*2*), and non-extracted (*3*) zeolite forms of clinoptilolite and of the extracted (*4*), extracted after reaction (*5*) and non-extracted (*6*) forms of MZ

Changes in the composition of clinoptilolite and of MZ after their extraction with acetylacetone and ion exchange are documented in Table IV. The Si/Al ratio increased from 4.20 to 5.21 in the activated clinoptilolite and from 1.52 to 2.48 in MZ, and the effectiveness of the extraction was only slightly higher for MZ. The changes of IR spectra of the original and extracted zeolitic forms are shown in Fig. 3. The slight splitting of a maximum at 1 085 cm^{-1} to 1 085 and 1 070 cm^{-1} occurs in clinoptilolite,

TABLE III
Product distribution (wt.%) in the initial stage (0) and after 30 min (30) methanol conversion (%) over several forms of clinoptilolite (for abbreviations see text)

Compound	Clinopt.		MZ		Extr. clinopt.		Extr. MZ	
	0	30	0	30	0	30	0	30
Methane	0.3	–	0.3	–	0.8	–	0.4	–
Ethylene	6.1	–	2.0	–	2.1	–	7.2	–
Ethane	1.4	–	0.8	–	0.8	–	3.7	–
Propylene	3.5	–	5.5	2.2	6.2	3.0	11.0	4.4
Propane	27.0	–	5.4	–	11.8	–	4.2	–
DME[a]	11.0	34.2	28.1	12.7	12.9	27.6	9.5	10.4
Butane	–	–	–	–	12.0	–	–	–
Conversion, %	94.9	45.9	79.9	29.3	90.0	44.3	71.1	28.6

[a] DME dimethyl ether.

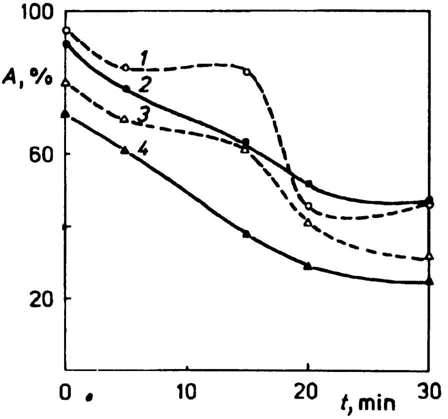

FIG. 4
Conversion of methanol *A* (in %) over clinoptilolite (*1*), the extracted clinoptilolite (*2*), MZ (*3*) and the extracted MZ (*4*) (for conditions see Experimental)

while the remaining part of the spectrum is not significantly different from the original one. In the MZ spectrum the reverse shift of band maximum occurs down to 1 070 cm^{-1} with a slight splitting at 1 055 cm^{-1}. The intensity of the 1 040 cm^{-1} band (related evidently to the Al content) decreases while some bands in the 800 – 620 cm^{-1} region disappear and the bands between 620 and 520 cm^{-1} merge. Positions of bridging hydroxyls or other OH groups in the extracted clinoptilolite remain unchanged, as shown in detail in Fig. 3. The disappearance of the 3 725 cm^{-1} band and an additional shift of the band of bridging OH groups to 3 630 cm^{-1} are observed for the extracted MZ.

Results of the catalytic reaction over the extracted zeolite forms (Table III) indicate the decrease of the conversion to 90.9% on clinoptilolite and to 71.1% on MZ. The amount of carbon deposits was 4.7 wt.% on clinoptilolite and 2.8 wt.% on MZ. DTA and TG analyses of extracted zeolite forms after the reaction (Fig. 5) indicate the pro-

TABLE IV
EDX microanalysis of clinoptilolite and of spherical MZ particles after the framework Al-extraction by 2,4-pentanedione

Zeolite	Content, wt.%						Si/Al molar ratio
	Na	Al	Si	K	Ca	Fe	
Clinopt.	1.19	14.21	77.31	1.10	0.5	5.79	5.21
MZ	2.10	27.21	70.69	–	–	–	2.48

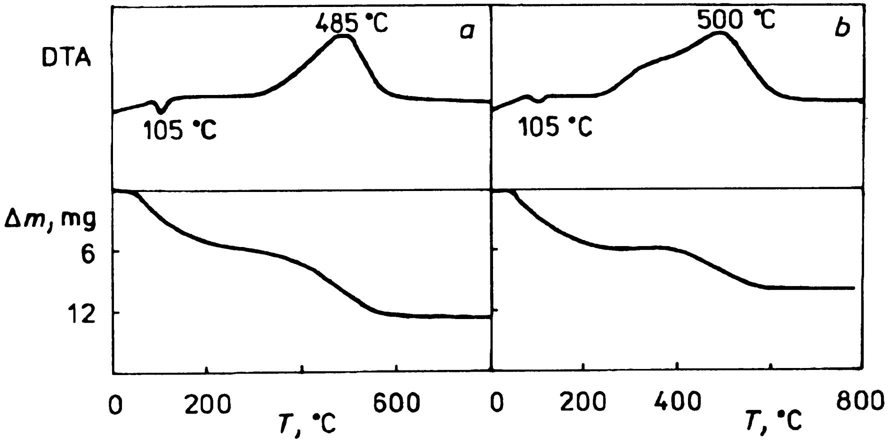

FIG. 5
DTA and TG analysis of the extracted clinoptilolite (*a*) and the extracted MZ (*b*) after the reaction

nounced weight loss at 105 °C, at the desorption of 5.7 wt.% of the physically bound water in the extracted clinoptilolite and 5.0 wt.% in the extracted MZ. The above results allow us to assume that a significant contamination of the surface cavities occurs mostly in clinoptilolite, preventing a process of water readsorption to take place. In comparison with the analyses of non-extracted zeolites before the reaction, one observes here a pronounced exo effect – at 485 °C in the extracted clinoptilolite with the 6.0 wt.% loss and at 500 °C in the extracted MZ with the 4.7 wt.% loss – related to the oxidation of possible desorption of carbonaceous fragments. Comparison of the total carbon contents and relevant weight losses suggests that this process involves the hydrocarbon residues adsorbed during the cracking process rather than carbon. Figure 5 shows that dehydroxylation of these zeolites was insignificant.

Comparison of IR spectra of extracted zeolites before and after the reaction (Fig. 3) indicates that the number of bands in the 800 – 500 cm^{-1} region has decreased, which could be related to the absence of some types of carbonaceous fragment vibrations.

The electron micrographs of the surfaces of the extracted zeolites are shown in Figs 6*a*, 6*b*. Comparison of the surface morphology of the extracted and non-extracted zeolite forms (Figs 1*a*, 1*b*) differing in their catalytic activity reveals only minor surface changes.

CONCLUSIONS

The modification of clinoptilolite by a high-aluminium synthetic zeolite reduces its initial catalytic activity in methanol conversion from 94.9 to 79.9 per cent. Although the initial activity of clinoptilolite is high, in the course of the catalytic process it becomes gradually depreciated, on account of the active sites deactivation by carbonaceous deposits. In continuing this work, modifications by other kinds of zeolites (low-aluminium ones) and the methods for reducing surface and cavity deactivation in the course of the reaction seem to be the most interesting items of further study.

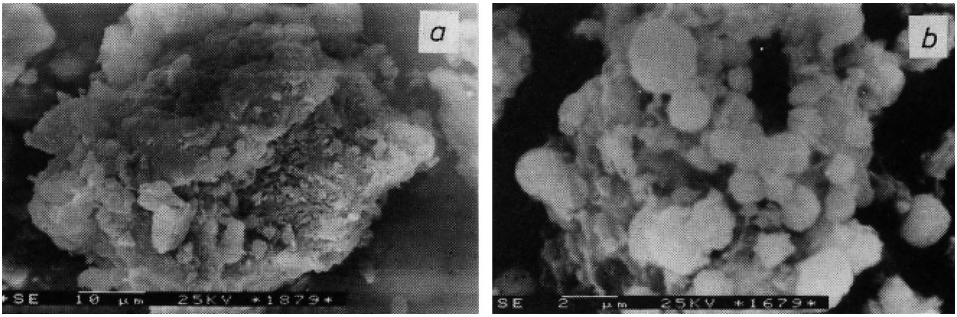

FIG. 6
Surface morphology of the extracted clinoptilolite (*a*) and the extracted MZ (*b*)

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