

Thermal decomposition of natural mordenite

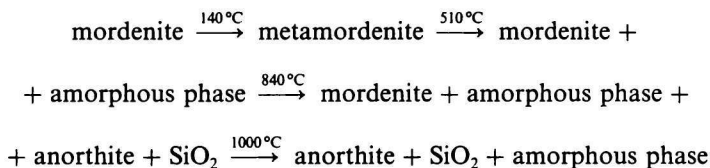
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Received 18 February 1985

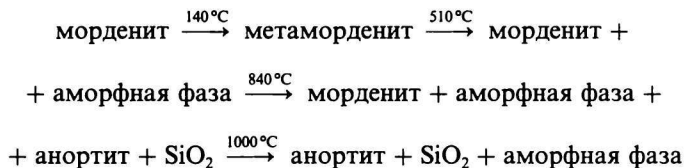
Accepted for publication 22 April 1986

The temperature stability of natural mordenite (Žďár by Stará Paka, Bohemia) was studied in the temperature range 20°C—1000°C both in dynamic regime in air (DTA, TG) and in isothermal regime *in vacuo*. The products of decomposition were investigated by the X-ray powder method and infrared absorption spectroscopy. The scheme of the decomposition of mordenite may be written as follows



Over the temperature of 510°C, the remaining water forms the structural hydroxyl groups which persist up to the highest temperatures.

Исследовалась термическая устойчивость природного морденита (Ждяр у Ст. Паки, ЧСР) в промежутке температур 20°C—1000°C как в динамическом режиме на воздухе (ДТА, ТГ), так и в изотермическом режиме в вакууме. Продукты разложения были исследованы рентгенографически порошковым методом и с помощью абсорбционной ИК-спектроскопии. Схему разложения морденита можно записать следующим образом



Начиная от температуры 510°C избыточная вода образует структурные гидроксильные группы, которые сохраняются до самых высоких температур.

According to *Breck* [1], mordenite appertains to the sixth structural group of zeolites. This mineral belongs among the zeolites with high content of silicon

(the ratio $n(\text{Si}) : n(\text{Al})$ always varies about the value of 5). This ratio indicates a well arranged distribution of Si/Al in structural positions of the framework. This framework consists of the chains containing five tetrahedrons which are joined with one another through bridge oxygen atoms to give 4-, 5-, 6-, and 8-membered rings. A high content of Si and energetically stable 5-membered rings predestine a high thermal stability of this mineral. There are two systems of channels in the framework. One of them is parallel with crystallographic direction [001] with entrance openings of 0.66 nm diameter while the second one is parallel with direction [010], the diameter of entrance openings being equal to 0.28 nm. The sodium and calcium atoms are localized in 8- and 12-fold positions of the structure and are coordinated to the molecules of water [2, 3]. The sodium atoms occur in the small channels (0.28 nm) while the calcium atoms are in the large channels (0.6 nm). The sodium ions in some positions are replaced by the potassium ions. Not only dehydration but also self-diffusion of cations into different holes of the structure takes place at increased temperatures. The activation energy of diffusion is $E_i = 36.57 \text{ kJ mol}^{-1}$ (Na), $29.87 \text{ kJ mol}^{-1}$ (K), and $43.72 \text{ kJ mol}^{-1}$ (Ca) [4]. These high values of activation energy of diffusion motion indicate the existence of repulsion-dispersion interactions of cations with neighbouring atoms of the framework. All these phenomena as well as the energetic barrier of the oxygen rings in the inlet openings of the channels and holes hinder the exchange processes between the cations in the holes of mordenite.

The aim of this study has been to determine the thermal stability of mordenite in the temperature range 100°C — 1000°C as well as the concomitant physico-chemical changes in the dynamic and isothermal regime of heating.

Experimental

The samples of natural mordenite (locality Žďár by Stará Paka, Bohemia) were obtained by separating the monomineral phase from the aggregates of fibrous monocrystals by using a microscope. The chemical analyses were performed in moist way by classical methods. The results of quantitative analysis are given in Table 1. The DTA and TGA curves were recorded with a derivatograph MOM (Radelkis, Budapest), system Paulik—Erdey, type G in air atmosphere by the use of the temperature program $10^\circ\text{C min}^{-1}$. The evaluation of results is presented in Table 2 and Figs. 1 and 2. The X-ray diffraction on polycrystalline samples of the products of thermal decomposition obtained under isothermal conditions was carried out with an X-ray diffractograph DRON-UM 1 by using $\text{CuK}\alpha$ -radiation ($\lambda = 0.15418 \text{ nm}$) and synthetic $\alpha\text{-Al}_2\text{O}_3$ as an internal standard. The measurements were performed in the range $2\theta = 0$ — 60° at laboratory temperature. The records of diffraction lines were evaluated according to the theoretical diffractograms [5]. The lattice parameters were calculated by means of the program MPIN [6]. The results are given in Tables 3—5.

Table 1
Chemical composition of mordenite ($w_i/\%$)

Oxide	Theoretical	Žďár
SiO ₂	62.85	63.80
Al ₂ O ₃	11.69	10.07
Na ₂ O	7.10	5.88
K ₂ O	—	1.46
CaO	—	2.33
MgO	—	1.68
MnO	—	0.19
Fe ₂ O ₃	—	1.40
TiO ₂	—	0.15
H ₂ O	12.36	12.79
	100.00	99.75
$n(\text{Si})/n(\text{Al})$	5.99	5.60
$n(\text{Si})/(n(\text{Si}) + n(\text{Al}))$	0.836	0.848

Table 2
Evaluation of TGA and DTA curves

Curve	$\theta/^\circ\text{C}$			
	360	640	785	1000
TGA	360	640	785	1000
DTA	140	510	840	1000
Total relative mass loss $-\Delta w/\%$	9.3	10.8	11.3	11.8
Increase in total relative mass loss $\Delta(-\Delta w)/\%$	9.3	1.5	0.5	0.5

The infrared absorption spectra of the products of isothermal decomposition were taken with a twin-beam spectrometer Perkin—Elmer, type 325. The samples were prepared in nujol suspension and measured in the range $\tilde{\nu} = 400\text{—}4000\text{ cm}^{-1}$ at laboratory temperature and pressure. The evaluation was based on literature data [1, 7]. The results are presented in Table 6 and Fig. 3.

The decompositions took place in a resistance furnace controlled by a thyristor regulator *in vacuo* (rotary oil pump) at numerical temperature values $\theta/^\circ\text{C} = 20, 140, 220, 265, 510, 840, \text{ and } 1000$. The temperature was taken with a thermocouple chromel—alumel. The decomposition finished, the samples were cooled *in vacuo* and suffused with nujol suspension. The preparations thus made were used for further study. The samples were held at individual temperatures for 3 h [8].

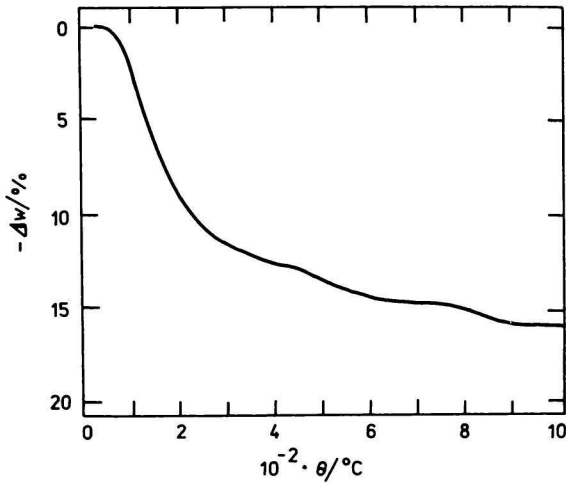


Fig. 1. TGA curve of natural mordenite.

Evaluation of TGA and DTA measurements

The TG and DTA curves (Figs. 1 and 2) show three stages of dehydration of natural mordenite. Consistently, we may see three steps in mass loss on the TG curve. The greatest step is in the temperature interval 20°C – 360°C and corresponds to the 9.3% mass loss. Further steps are in the temperature intervals 360°C – 640°C (1.5 mass %) and 640°C – 785°C (0.5 mass %). Up to 1000°C , mordenite still loses about 0.5% of mass, so that this mineral loses altogether 11.8% of mass in the temperature range 20°C – 1000°C . According to chemical analysis, mordenite contains 12.79 mass % of water

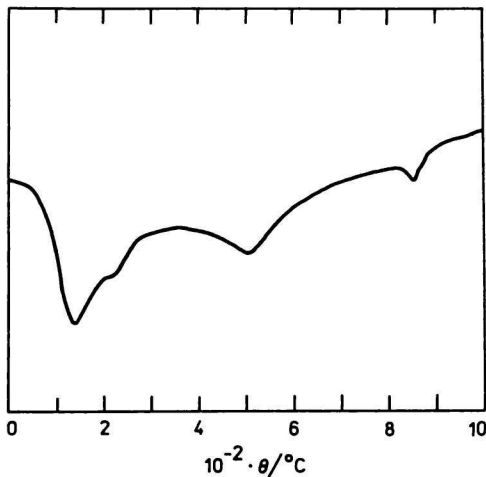


Fig. 2. DTA curve of natural mordenite.

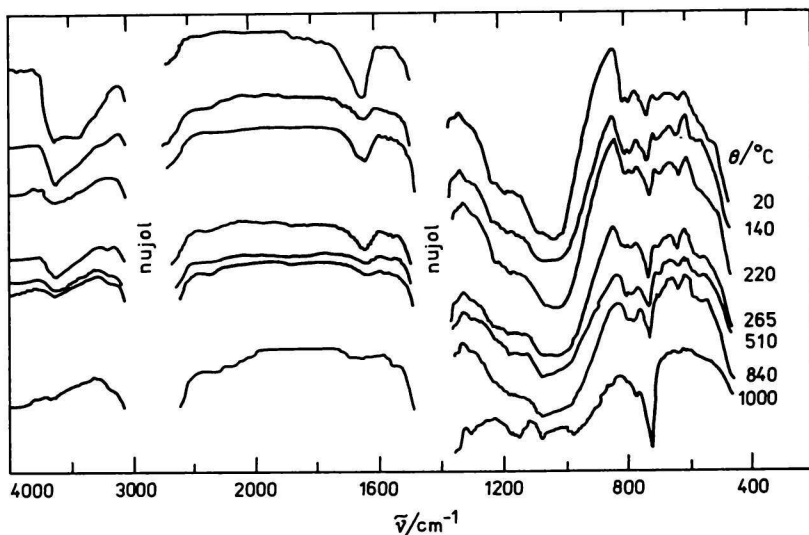


Fig. 3. Infrared spectra of the products of isothermal decomposition of mordenite. Perkin—Elmer, type 325, nujol suspension, wavenumber range $\tilde{\nu} = 400\text{--}4000\text{ cm}^{-1}$.

which is localized in the holes of the mineral together with cations. It means that 0.99 mass % of water still remains in the mineral after thermal treatment. This residual water might be bonded through the hydroxyl groups to the Al—O⁽⁻⁾—Si bridges. The DTA curve exhibits only three endothermic peaks (Table 2, Fig. 2). The most conspicuous maximum occurs at 140 °C while the others at 510 °C and 840 °C are weaker. These peaks indicate gradual dehydration involving the water molecules present in different structural positions. Thus we may assume that the water molecules coordinated to the Ca²⁺ ions and present in large holes are predominantly liberated in the temperature interval 20 °C—360 °C. In the second stage (at about 500 °C), the remaining water molecules coordinated to the Ca²⁺ ions are liberated and the dehydration involving the water molecules coordinated to the Na⁺ ions in small holes begins. In the third stage (at about 840 °C), the rest of free water molecules escapes from small holes. These last two steps of dehydration may be accompanied by migration of the Na⁺ ions into large holes of the mineral where the heterolytic reaction between cations and water molecules takes place. The liberated protons immediately attack the oxygen atoms in the Al—O⁽⁻⁾—Si bridges to give the structural hydroxyl groups (see discussion about infrared spectra). That process brings about impairment of the bonds in these bridges and at higher temperatures even breakage of these bonds. In this way, some tetrahedral fragments of structure may arise in the amorphous phase.

Table 3
X-Ray diffraction patterns of the decomposition products of mordenite

<i>hkl</i>	<i>Breck</i> [1]		20 °C		140 °C		220 °C		265 °C		510 °C		840 °C	
	<i>d/nm</i>	<i>I</i> _{rel}	<i>d/nm</i>	<i>I</i> _{rel}	<i>d/nm</i>	<i>I</i> _{rel}	<i>d/nm</i>	<i>I</i> _{rel}	<i>d/nm</i>	<i>I</i> _{rel}	<i>d/nm</i>	<i>I</i> _{rel}	<i>d/nm</i>	<i>I</i> _{rel}
110	1.352	42	—	—	—	—	—	—	—	—	—	—	—	—
120	1.019	7	—	—	—	—	—	—	—	—	—	—	—	—
200	0.903	100	0.905	90	0.912	80	0.915	80	0.900	80	0.905	82	0.905	60
220	0.677	4	0.670	10	0.665	10	0.669	15	0.660	15	0.658	10	0.640	5
111	0.657	8	0.655	15	0.660	10	0.660	10	0.655	10	—	—	0.628	80 Q + An
130	0.638	37	0.630	30	0.628	25	0.630	25	0.628	25	0.625	20	—	—
021	0.606	3	0.604	10	0.602	8	0.605	8	0.600	10	0.600	8	0.620	15
310	0.578	28	0.580	20	0.580	20	0.582	20	0.578	20	0.570	20	—	—
											0.465	10 Q	0.565	10
330	0.451	42	0.453	40	0.450	35	0.452	35	0.450	30	0.448	25	0.465	30 Q
											0.409	50 Q	0.440	15
041	0.426	6	0.429	5	0.430	5	0.430	5	0.425	2	—	—	0.409	60 Q
420	0.4133	9	0.415	10	0.410	5	0.416	10	0.410	10	0.408	8	—	—
150	0.3980	100	0.3985	95	0.3980	90	0.3982	95	0.3978	95	0.3972	90	0.3970	80

Table 3 (Continued)

<i>hkl</i>	20°C		140°C		220°C		265°C		510°C		840°C	
	<i>d</i> /nm	<i>I</i> _{rel}	<i>d</i> /nm	<i>I</i> _{rel}	<i>d</i> /nm	<i>I</i> _{rel}	<i>d</i> /nm	<i>I</i> _{rel}	<i>d</i> /nm	<i>I</i> _{rel}	<i>d</i> /nm	<i>I</i> _{rel}
241	0.3830	5	0.3840	10	0.3840	10	0.3838	8	0.3845	5	—	—
002	0.3757	8	0.3760	15	0.3759	15	0.3752	10	0.3758	15	0.3760	10
510	0.3563	14	0.3568	15	0.3565	15	0.3560	10	0.3562	15	0.3568	10
151	0.3528	3	0.3530	5	—	—	—	—	—	—	—	—
202	0.3471	24	0.3475	30	0.3472	30	0.3468	25	0.3470	25	0.3475	20
060	0.3410	23	0.3405	25	0.3403	25	0.3400	25	0.3400	20	0.3395	10
350	0.3386	44	0.3385	40	0.3383	35	0.3384	30	0.3375	30	0.3370	20
511	0.3218	24	0.3220	25	0.3220	20	0.3215	15	0.3210	10	—	—
260	0.3198	35	0.3195	40	0.3195	40	0.3190	40	0.3194	35	0.3195	—
261	0.2939	3	0.2941	5	0.2943	5	0.2945	2	—	—	—	—
332	0.2891	11	0.2890	10	0.2890	10	0.2882	8	—	—	—	—
550	0.2710	2	—	—	—	—	—	—	—	—	—	—
171	0.2697	33	0.2695	30	0.2695	30	0.2690	25	0.2695	25	0.2698	20
									0.2135	40 Q	0.2136	80 An + Q

Table 4

Evaluation of X-ray diffraction patterns of the decomposition products of mordenite after isothermal heating to 1000 °C

d/nm	I_{rel}	Found phase
0.900	30	Mordenite
0.628	100	Quartz + anorthite
0.524	20	Anorthite
0.440	10	Mordenite
0.465	25	Quartz
0.4095	60	Quartz
0.4075	40	Quartz
0.3475	10	Mordenite
0.3208	20	Anorthite
0.3164	30	Anorthite
0.2949	10	Anorthite
0.2884	20	Anorthite
0.2528	25	Anorthite
0.2136	80	Quartz + anorthite
0.2027	25	Anorthite
0.1467	10	Anorthite

Table 5

Parameters a , b , c as a function of temperature

20 °C	$a = (1.811 \pm 0.004) \text{ nm}$ $b = (2.046 \pm 0.005) \text{ nm}$ $c = (0.754 \pm 0.002) \text{ nm}$
140 °C	$a = (1.818 \pm 0.005) \text{ nm}$ $b = (2.049 \pm 0.005) \text{ nm}$ $c = (0.755 \pm 0.003) \text{ nm}$
220 °C	$a = (1.819 \pm 0.005) \text{ nm}$ $b = (2.051 \pm 0.005) \text{ nm}$ $c = (0.757 \pm 0.003) \text{ nm}$
265 °C	$a = (1.807 \pm 0.005) \text{ nm}$ $b = (2.038 \pm 0.005) \text{ nm}$ $c = (0.750 \pm 0.002) \text{ nm}$
510 °C	$a = (1.813 \pm 0.004) \text{ nm}$ $b = (2.049 \pm 0.005) \text{ nm}$ $c = (0.753 \pm 0.005) \text{ nm}$
1000 °C	$a = (0.818 \pm 0.003) \text{ nm}$ anorthite $b = (1.288 \pm 0.003) \text{ nm}$ $c = (1.417 \pm 0.002) \text{ nm}$

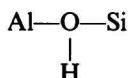
Evaluation of X-ray diffraction of the decomposition products

It results from evaluation of the X-ray powder diffraction patterns of the products of thermal decomposition of natural mordenite that the crystal structure of this mineral is stable up to 510 °C. In the temperature range 20 °C—510 °C only the process of dehydration proceeds and the lattice parameters change (Table 5). Beyond 510 °C, we may observe a partial decay of mordenite giving rise to quartz and amorphous portion (Table 3) which is likely to contain certain segments of the tetrahedral groups with short-range order. Of course, a certain portion of mordenite remains preserved even at 840 °C. Notwithstanding, its diffraction pattern is different from that of original mineral (Table 3). Beyond this temperature, a mixture of anorthite and silicon dioxide originates from the amorphous phase and the rest of nondecomposed mordenite (Table 4). The formation of this mixture is finished at 1000 °C. At this temperature, the X-ray diffraction patterns of both these substances appear with small peaks of nondecomposed mordenite on high background (maybe due to the amorphous phase).

Evaluation of infrared spectra of the decomposition products

We can observe the asymmetric and symmetric stretching vibrations of the OH groups in all spectra up to 810 °C. Under the temperature of 510 °C the bands of the bending vibration of H—O—H are also present in the infrared spectra.

The bands of different intensities and structures of the asymmetric and symmetric T—O (T = Si, Al) and T—O—T vibrations (wavenumber range $\tilde{\nu} = 1180\text{--}720\text{ cm}^{-1}$), torsional T—O—T vibration (wavenumber range $\tilde{\nu} = 690\text{--}520\text{ cm}^{-1}$) and bending O—T—O and T—O—T vibrations (wavenumber range $\tilde{\nu} = 460\text{--}450\text{ cm}^{-1}$) are present in all spectra up to 1000 °C. Therefore we may deduce that the dehydration proceeds up to 510 °C and beyond this temperature the structural hydroxyl groups arise in the



bridge and continue to exist up to 840 °C. We can infer from the vibrations of the T—O, O—T—O, and T—O—T bonds which are present in the spectra of all decomposition products that the order in the Si(Al)O₄ tetrahedrons does not change within the whole temperature range and only deformations of bonds and angles appear.

Conclusion

The overall scheme of the decomposition of mordenite may be written as follows

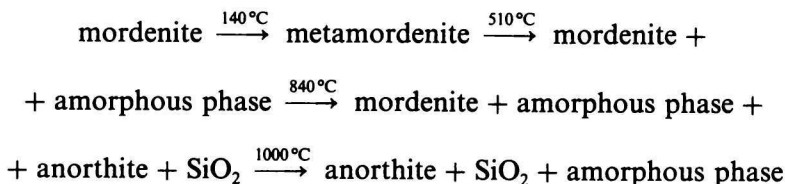


Table 6
Evaluation of infrared spectra of the decomposition products of mordenite

Assignment	$\tilde{\nu}/\text{cm}^{-1}$						
	20 °C	140 °C	220 °C	265 °C	510 °C	840 °C	1000 °C
Antisymmetric and symmetric stretching vibration	3700 vw	3700 vw	3700 vw	—	—	—	—
	3610 s	3615 m	3615 m	3610 s	3610 w	3610 s	—
	3420—3480 s	—	—	—	—	—	—
	—	3190 vw	3190 vw	—	—	—	—
Bending H ₂ O vibration	1635—1650 s	1630 m	1640 m	1630 m	1620—1650 w	—	—
Antisymmetric TO ₄ + T—O—T vibration	1180 vw	1180 vw	1180 vw	1180 vw	1180 vw	1180 vw	1180 vw
	1000—1080 vs	1000—1080 vs	1000—1080 vs	980—1070 vs	990—1070 vs	970—1070 vs	1170 w 1150 splitting 1070 w 990 w 970 vw 960 vw 930 vw 890 w
Symmetric T—O + T—O—T vibration	800 m	800 m	800 m	800 w	800 w	790 w	770 w
	780 splitting	780 splitting	780 splitting	780 w	780 w	775 w	—
	725 m	725 m	725 m	720 w	720 m	720 m	720 s

Table 6 (Continued)

Assignment	$\bar{\nu}/\text{cm}^{-1}$						
	20°C	140°C	220°C	265°C	510°C	840°C	1000°C
Torsional	690 w	690 w	690 w	690 w	690 w	690 vw	690 infl
T—O—T	620 w	630 w	630 w	630 w	630 w	630 w	630 vw
vibration	—	560 vw	560 vw	560 vw	560 vw	580 w	580—540 vw
	—	—	—	—	560 splitting	—	—
	520 vw	—	—	—	—	—	—
Bending	460 vs	460 vs	460 vs	450 s	450 s	450 s	450—460 m
T—O + T—O—T							
vibration							

vw — very weak, w — weak, m — medium, s — strong, vs — very strong; T = Si, Al.

It ensues from the preceding discussion that mordenite is not subjected to great structural changes in the course of dehydration and is stable approximately to 600 °C. Then the crystal structure is destroyed and the amorphous phase comes into existence. At the temperature of 800 °C a mixture of anorthite and SiO₂ starts to arise. This formation is terminated approximately at 1000 °C. (A small amount of the nondecomposed mordenite persists even at this temperature.) For this reason, mordenite may be used as a carrier of catalysts up to the temperature of about 500 °C and is also applicable as a molecular sieve at increased temperatures.

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Translated by R. Domanský