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HYDROTHERMAL DECOMPOSITION OF VANADIUM GLASSES

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The effect of 2M solutions of alkali hydroxides and carbonates on vanadium glasses at 90 °C and under hydrothermal conditions at 180 °C were studied. X-ray analysis and scanning electron microscopy showed that in dependence on the composition of the glasses and the solutions, the hydrothermal decomposition at 180 °C yields analcime, feldspars, foids, clay minerals and cancrinite The reactions at lower temperature (90 °C) produced, apart from sodalite, above all the zeolitic phases phyllipsite, chabazite, analcime and synthetic zeolites P_C, A, KH and F. The crystales of the products insofar as they were wel identifiable by electron microscopy, were analyzed for the content for vanadium: the highest content was found in analcime (3—10%), zeolites A and H (1—2%) and virtually no vanadium was determined in phlillipsite and synthetic zeolite P_C (< 1%).

INTRODUCTION

The present study is a part of an extensive programme [1] whose aim was to investigate the possibility of preparing zeolites containing a vanadium heteroatom in their structure (3rd generation zeolites) by means of hydrothermal conversion of vanadium glasses. Zeolites of the third generation are at present subject of considerable interest because of their wide application possibilities in technological practice, first of all as catalysts for organic and inorganic syntheses and redox reactions. Some inorganic vanadium compounds are known to exhibit efficient catalytic properties, particularly with respect to oxidative and reduction reactions. The radius of the pentavalent vanadium cation conforms to Pauling's criterium for isomorphous substitution of silicon cations in mutation.

The present authors started to deal with the introduction of transient metal atoms into lattice of the zeolites in the early seventie [2]. The existing methods used in the preparation of this type of catalyst can be divided into the following three groups:

1. Impregnation and ionic exchange [3, 4, 5, 6, 7].
2. Melting the zeolite with compounds of transient elements [8, 9].
3. Preparation of the zeolites from gels or sols of oxides or other inorganic compounds of the basic elements (including transient metals [10—16]).

In the first case, the active component is allowed to combine with a natural or synthetic zeolite. In the other two instances the oxides or other inorganic compounds are introduced directly into the reaction mixture prior to the actual preparation of the zeolite.

The pisitions of the transient metal atoms in the structure of the zeolites were mostly no determined by the respective authors, owing to the difficulties involved in the experimental works. Levina et al. [17] point out that with respect on the catalytical effects it is irrelevant whether the transient metal atom has substituent an aluminum or a silicon atom in the zeolitic structure, or whether it is built in ionic position or in a structural void. The same catalytic effect is exhibited, according to the authors, by zeolites in which the respective transient metal atom is only adsorbed in the surface of the zeolite in the form of an inorganic salt. Similarly, Habesberger et al. [18] say that a metal built into the silicon positon has a positive effect on acidobasic catalysis whereas oxidation-reduction reactions require the presence of an ion occurring in more than one valency, regardless of its position.

EXPERIMENTAL

Vanadium glasses were melted at 1500—1700 °C at the State Glass Research Institute in Hradec Králové, from batches prepared by mixing the compounds Al_2O_3 (chromatography grade, Real Budapest), SiO_2 (high-purity synthetic crystal), NH_4VO_3 A.R. and Na_2CO_3 A.R. (Lachema Brno). The proportions of the oxides percent by weight were varied according to Table I. Soda was added in a constant amount as flux. The glasses obtained were ground to analytical finesess (200 mesh) and analyzed for the content of Al, Si, Na nad V (the EDAX method, auxiliary device for the JXA-50 A microprobe by Jeol). The results and the calculated contents of the given oxides are listed in Table II. X-ray analyses of the glasses showed them to be amorphous in character.

Table I

Calculated content of Al_2O_3, SiO_2 and V_2O_5 in the glasses [Na_2O content not included]

Glass	Al_2O_2 %	SiO_2 %	V_2O_5 %
Va-1	20	80	0
Va-3	20	60	20
Va-5	20	40	40
Va-7	30	70	0
Va-9	30	50	20
Va-11	30	30	40
Va-13	40	60	0
Va-15	40	40	20
Va-17	40	20	40
Va-19	50	50	0
Va-21	50	30	20
Va-23	50	10	40

The glasses were treated hydrothermally for 4 days, in agitated glass flasks placed in a water thermostat at 90 °C and under atmospherical pressure, or in steel autoclaves at 180 °C under the pressure of saturated vapours (at 70 % autoclave capacity, this amoundted to approx. 0.99 MPa). The internal pressure was calculated from the P—V—T thermodynamic relationship of the given system. In the calculations, use was made of values for pure water (19) which correspond, with satisfactory accuracy, to dilute solutions of inogranic compounds. The deviations from the absolute value amount to the orede of several percent and are well i-thin the range of experimental errors [20, 21]. The design of the autoclaves employed is described in detail in [22]. The capacity of the autocalves was about 20 ml. The autoclaves were filled at a constant solid to liquid ratio of 1 : 6.

Table II

Chemical composition of the glasses

Glass	Na_2O (wt. %)		Al_2O_3 (wr. %)		SiO_2 (wt. %)		V_2O_5 (wt. %)		Total %
	Edax	calc.	Edax	calc.	Edax	calc.	Edax	calc.	
Va-1	13.0	16.84	16.9	16.63	70.1	66.53	0	0	100
Va-3	15.4	16.99	14.7	16.78	54.2	50.34	15.7	15.89	100
Va-5	15.0	17.08	14.0	16.87	39.6	33.74	31.3	32.32	100.01
Va-7	14.3	16.84	25.5	24.94	60.35	58.21	0	0	100
Va-9	14.9	16.99	25.7	25.17	43.6	41.95	15.8	15.89	100
Va-11	15.1	17.08	23.2	25.3	28.9	25.3	32.8	32.32	100
Va-13	14.8	16.84	30.2	33.27	55.0	49.90	0	0	100.01
Va-15	14.2	16.99	30.1	33.56	36.1	33.56	15.7	15.89	100
Va-17	15.9	17.08	31.7	33.74	21.4	16.87	31.1	32.32	100.1
Va-19	13.9	16.84	39.7	41.58	46.4	41.58	0	0	100
Va-21	14.2	16.99	38.5	41.95	30.8	25.17	16.5	15.89	100
Va-23	15.3	17.08	39.0	42.17	14.2	8.43	31.2	32.32	100

Explanatory notes:

Edax — values determined analytically by means of electron microprobe

calc. — values calculated from the weighed-in amounts of the individual oxides

The glasses were decomposed at 180 °C in a medium of 2 M solutions of Na_2CO_3, K_2CO_3 nad NaOH, respectively and at 90 °C, addition to these, in a mixed 2M solution of NaOH + KOH (molar ratio 1 : 1).

After removal from the reaction vessels, the reaction products were repeatedly decanted with 1 M hydrochloric acid and 1 M solution of sodium perchlorate to eliminate the vanadium absorbed in the surface ot the products, then with distilled water, and finally dried at room temperature.

The individual phases of the hydrothermal decomposition products were identified by X-ray analysis and by scanning electron microscopy (Tables III and IV). The former were carried out on the Chirana diffractograph (CuK_α radiation, Ni filter). The phases were identified by means of X-ray diffraction tables [23, 24] and the database for zeolite X-ray patterns (Institute of Mineral Raw Materials, Kutná Hora); The latter analyses made use of the secondary electron method and the JXA — 50 A Jeol scanning electron microscope. The micrographs of the crystalline phases at 600—5000 x magnification are shown in Figs. 8—15. The micrographs were also compared with those of zeolitic crystals published in [23, 25]. The identified zeolites were also analyzed by the EDAX electron microprobe method for the content of Al, Si, Na, K and V (Table 5).

DISCUSSION OF THE RESULTS

Decompostititon of vanadium glasses at 90 °C

At 90 °C, the vanadium glasses were always treated for a period of 4 days in 4 M solutions of Na_2CO_3, NaOH, K_2CO_3 and a mixed NaOH + KOH solution (molar ratio 1 : 1).

Table III

The products of hydrothermal treatment of vanadium glasses at 90 °C

Glass	Medium			
	2 M Na_2CO_3	2 M K_2CO_3	2 M NaOH	2 M NaOH + KOH
Va-1	zeol. P_C	leucite	zeol. P_C	phillipsite, chabazite
Va-3	natrolite, zeol. P_C	leucite	zeol. P_C	phillipsite
Va-5	natrolite, zeol. P_C	*K*-sodalite, leucite	zeol. P_C	phillipsite
Va-7	zeol. P_C	leuite, cristobalite	zeol. P_C	chabazite, nepheline
Va-9	zeol. P_C	*K*-sodalite	zeol. P_C	phillipsite
Va-11	sodalite	*K*-sodalite, phillipsite	zeol. P_C	phillipsite, zeol. *F*
Va-13	zeol. P_C	phillipsite	zeol. P_C	chabazite, phillipsite
Va-15	analcime, zeol. P_C	*K*-sodalite, phillipsite	zeol. P_C	phillipsite, zeol. KH
Va-17	sodalite	*K*-sodalite, phillipsite	zeol. P_C, zeol. *A*	zeol. *F*
Va-19	zeol. P_C, chabazite	*K*-sodalite, phillipsite	zeol. P_C, chabazite	phillipsite, chabazite
Va-21	sodalite	*K*-sodalite	zeol. P_C, hydroxysodalite	phillipsite, zeol. *KH*
Va-23	sodalite	zeol. *F*	hydroxysodalite	hydroxysodalite, zeol. *F*

The minerals found in the productes of the individual experiments are listed in Table III and plotted in the tree-component system Al_2O_3—SiO_2—V_2O_5 (the content of Na_2O was identical in all of the glasses). The respective diagrams expressing the occurence regions of the individual mineral phasses in the decomposition products in terms of the initial composition of the vanadium glasses, are shown in Figs 1—4. The boundaries of the same decomposition products indicated by the lines in the diagrams cannot be regarded as regions of kinetic stability of the individual phases (insufficient data available for such a purpose); they only demacate the occurence of the mineral phases in the experiments in a comprehensive way.

Under the given experimental conditions, for the 2 M soda solution and glasses with $Al_2O_3/SiO_2 > 1$, and in the presence of V_2O_5 in the glass, the decomposition yielded mostly sodalite, white at $Al_2O_3/SiO_2 < 1$ it was jointly with natrolite [24] at the lowest Al_2O_3 content, chabasite [24] (with glasses free of V_2O_9) or analcime [24].

In the medium of 2 M NaOH solution, zeolite P_C was formed almost all over the concentration range studied (Fig. 2). Hydroxysodalite resulted from the decomposition of only two vanadium glasses with the highest alumina content. De-

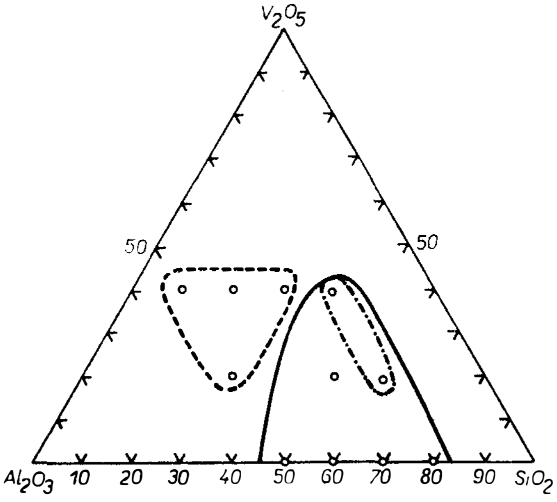

Fig. 1. Three-component diagram. Occurence of mineral phases in the products of hysrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses.*

90 °C, 2 M Na_2CO_3

———————— *zeolite* P_C

— — — — *sodalite*

— . — . — *natrolite.*

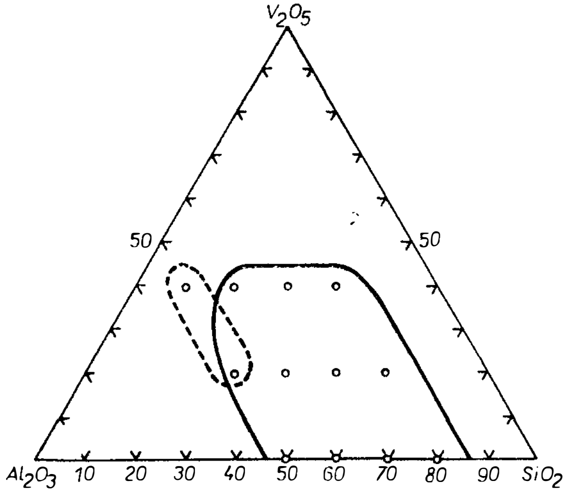

Fig. 2. Three-component diagram. Occurence of mineral phases in the products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses.*

90 °C, 2 M NaOH

———————— *zeolite* P_C

—— - - - —— *sodalite*

◑ *zeolite A*

◓ *chabazite.*

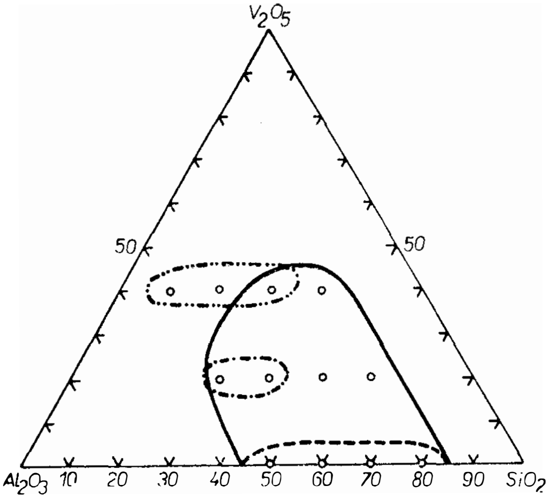

Fig. 3. Three-component diagram. Occurence of mineral phases in the products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses.*

90 °C, 2 M (NaON + KOH)

———————— *phillipsite*

—— —— —— *chabazite*

—— · —— *zeolite KH*

—— · · —— *zeolite F.*

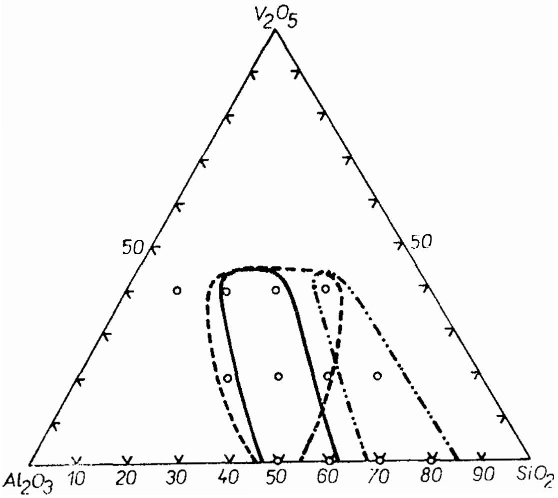

Fig. 4. Tree-component diagram. Occurence of mineral phases in the products of hydrothermal decomposition vs. the content of SiO_2, Al_1O_3 *and* V_2O_5 *on the glasses.*

90 °C, 2 M K CO_3

———————— *phillipsite*

— — — — *K sodalite*

—— · —— *leucite*

◑ *zeolite F.*

compostiton for glasses with a lower SiO_2 content yielded zeolite P_C and chabazite [24] (in the absence of vanadium), and zeolite *A* [23] (from glasses with the highest content of V_2O_5).

Phillipsite was formed in almost all instances in the medium of the mixed NaOH and KOH solution and in that of sodium hydroxide alone [24]. The vanadium-free glasses were converted to phillipsite and chabazite, and those with a medium content fo SiO_2 and V_2O_5 to synthetic zeolite *KH* [23]. In some cases, nepheline and sodalite also found jointly with phillipsite (Fig. 3). Decomposition of glasses with the highest V_2O_5 content and a medium to low SiO_2 content yielded synthetic potassium zeolite *F* [23].

Decomposition of vanadium glasses in 2 M K_2CO_3 solution at 90 °C yielded leucite [27], phillipsite, *K*-sodalite and zeolite *F* as the main products (Fig. 4). Glasses with higher SiO_2 contents were converted to the potassium analogue of analcime- leucite, and the range of phillipsite formation was thus shifted towards higher alumina content in the glasses and virtually joined the sodalite occurence range (unlike the case of solutions with sodium ions, sodium-potassium sodalite was formed, further on designated *K*-sodalite), and both mineral phases were mostly produced at the same time. Synthetic zeolite *F* was the main product of decomposition of glasses with a low SiO_2 content and a high Al_2O_3 and V_2O_5 content, similary to the case of the mixed NaOH + KOH solution.

Conversion of vanadium glasses at 180 °C

As follows from the three-component diagram in Fig. 5, decomposition of the glasses with higher SiO_2 content yields analcime, that of glasses with a lower content producing clay minerals (montmorillonite or kaolinite) regardless of the vanadium content in the glasses. Roughly at the center of the field, the middle ratio of the $SiO_2 : Al_2O_3$ oxides, cancrinite is also present apart from the phases mentioned.

The hydrothermal treatment in 2 M NaOH solution produced similar results except that the regions of the individual mineral phases were somewhat shifted (Fig. 6).

Clay minerals are again formed in the medium containing the potassium ion (2 M K_2CO_3) from glasses with a low $SiO_2 : Al_2O_3$ ratio. Those with the medium ratio produced calsilite or tricalsilite. Glasses with the highest SiO_2 content yielded potassium feldspars, mostly jointly with another mineral phase (nepheline from glasses containing V_2O_5, leucite from glasses free of vanadium).

Phillipsite (or zeolite P_C), sodalite and analcime (in potassium media its *K* derivative, leucite) were the most frequent products of hydrothermal treatment of glasses at 90 °C. In sodium-containing media, also natrolite, chabazite, and synthetic zeolite *A* were formed; in the potassium-contaning media, nepheline, chabazite and synthetic zeolites *KH* and *F* were produced. Hydrothermal treatment at 90 °C therefore yielded above all zeolites. These were analyzed for their vanadium content (Table V) in order to study the possibility of preparation of vanadium zeolites by hydrothermal decomposition of vanadium glasses. The content of Al, Si, Na and K, and particularly that of V was determined in selected samples containing well identifiable zeolitic crystals. The values listed in Table V are means of at least 6 analyses and have been corrected by means of a standard (jadeite). The analyses showed that vanadium was virtually not bound in the structure

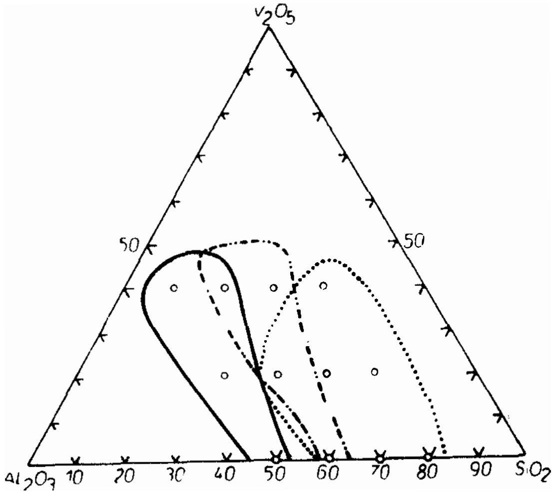

Fig. 5. Three-component diagram. Occurence of mineral phases in the products of hydrothermal decomposition vs. the content of SiO_2*,* Al_2O_3 *and* V_2O_5 *in the glasses.*

180 °C, 2 M Na_3VO_3

———————— *clay mineral*

——— ——— . . *cancrinite*

. . . . *analcime.*

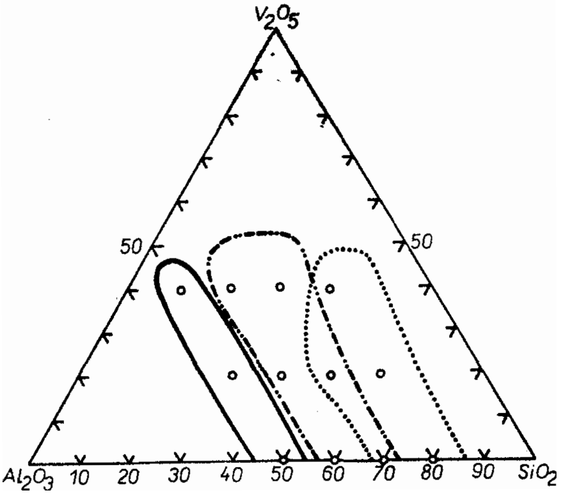

Fig. 6. Three-component diagram. Occurence of mineral phases in the products of hydrothermal decomposition vs. the content of SiO_2*,* Al_2O_3 *and* V_2O_5 *in the glasses.*

180 °C, 2 M K_2CO_3

———————— *clay mineral*

——— ——— . . *cancrinite*

. . . . *analcime.*

Table IV

The products of hydrothermal treatment of vanadium glasses at 180 °C

Glass	Medium		
	2 M Na_2CO_3	2 M K_2CO_3	2 M NaOH
Va-1	analcime	*K*-feldspar	analcime
Va-3	analcime	*K*-feldspar	analcime
Va-5	analcime	calsilite	analcime
Va-7	analcime	leucite, *K*-feldspar	analicime, cancrinite
Va-9	analcime	tricalsilite	analcime, cancrinite
Va-11	cancrinite	calsilite	cancrinite
Va-13	analcime, cancrinite	leucite, *K*-feldspar	cancrinite
Va-15	analcime, cancrinite	calsilite	cancrinite
Va-17	cancrinite, clay mineral	clay mineral	cancrinite
Va-19	clay mineral	leucite, calsilite	clay mineral
Va-21	clay mineral	clay mineral	clay mineral
Va-23	clay mineral	clay mineral	clay mineral

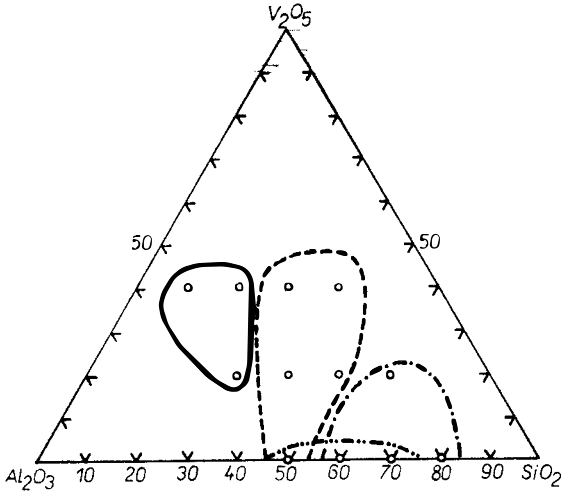

Fig. 7. Three-component diagram. Occurence of mineral phases in the products of hydrothermal decomposition vs. the content of SiO_2, Al_2l_3 *and* V_2O_5 *in the glasses.*

180 °C, 2 M K_2CO_3

———————— *clay mineral*

— — — — *calsilite* (*tricalsilite*)

—— . . ——— *leucite*

——- . ——— *K feldspar.*

of phillipsite and zeolite P_C where only tenths of a percent were determined. A vanadium content of about 1% was found in synthetic zeolites *A* and *F*. Quite high vanadium concentrations were established in samples of sodalite (2—14%) and analcime (3—10%). No distinct shift in the d values in the diffraction patterns was observed.

Table V

Content of Na, K, Al, Si and V in the products of hydrothermal treatment of vanadium glasses

Mineral	Conditions of treatment	Content of the element in the mineral (wt. %)				
		Na	K	Al	Si	V
sodalite	Va-17, Na_2CO_3, 90 °C	20	—	32	43	4
	Va-21, Na_2CO_3, 90 °C	17	—	28	45	10
	Va-23, Na_2CO_3, 90 °C	17	—	31	44	8
hydroxysodalite	Va-23, NaOH, 90 °C	18	—	32	45	5
	Va-23, NaOH + KOH, 90 °C	13	—	32	46	9
K-sodalite	Va-15, K_2CO_3, 90 °C	14	3	26	47	14
	Va-21, K_2CO_3, 90 °V	15	4	30	39	11
zeolite P_C	Va-9, NaOH, 90 °C	17	—	32	51	<1
	Va-15, NaOH, 90 °C	16	—	33	51	<1
	Va-19, NaOH, 90 °C	20	—	26	53	1
phillipsite	Va-5, NaOH + KOH, 90 °C	7	15	27	50	1
	Va-9, NaOH + KOH, 90 °C	8	16	27	49	<1
	Va-19, NaOH + KOH, 90 °C	12	8	29	50	0
analcime	Va-15, Na_2CO_3, 90 °C	13	—	16	58	10
	Va-5, Na_2CO_3, 180 °C	13	—	21	63	3
	Va-7, Na_2CO_3, 180 °C	15	—	23	55	7
zeolite *F*	Va-11, NaOH + KOH, 90 °C	3	29	25	42	1
	Va-17, NaOH + KOH, 90 °C	7	26	28	37	2
	Va-23, K_2CO_3, 90°C	5	25	24	45	1
zeolite *A*	Va-17, NaOH, 90 °C	19	—	32	45	1—2

The temperature of 180 °C was proved excessively high for hydrothermal preparation of zeolites (with the exception of analcime). The sodium media produced above all analcime, cancrinite, clay minerals and nehpeline, the potassium ones calsilite and potassium feldspars.

Glasses generally can be suitable materials for the preparation of zeolites by hydrothermal decomposition at lower temperatures. The transient element (vanadium) present in glass in higher concentration (> 10%) passes more readily into the structure of some zeolites than by other methods of preparation mentioned in the theoretical part of the present paper.

CONCLUSION

Hydrothermal decomposition of vanadium glasses on basic media at the higher temperature employed (180 °C) yielded analcime, feldspars, feldspatoids and clay minerals. The same treatment at lower temperature (90 °C) produced mainly sodalite and zeolites. In the medium of NA^+ ions it was mostly zeolite P_C, less frequently natrolite, chabazite nad zeolite A. The medium of K^+ ions that of mixed $Na^+ + K^+$ ions gave rise to phillipsite, to a lesser degree to chabazite, zeolites *F* and *KH*.

The vanadium originally contained in the glasses passed most quantitatively into analcime (up to 10%) and sodalite (up to 14%), less into zeolite *KF* (2%) and zeolites *A* and *F* (1%).

With respect to their composition, structure and high degree of homogenitu, glasses are suitable materials for hydrothermal preparation of some synthetic minerals. Hydrothermal treatment at lower temperature (about 100 °C) in basic media can be used to produce synthetic zeolites which are nowdays in high demand. Promising results have been obtained in the preparation of zeolites containing vanadium, even though the present authors were unable to determine the position taken up by the vanadium atoms in the structure. However, the vanadium was not merely absorbed in the zeolite surface, as proved by the multiple decantation with HCl and $NaClO_4$. Vanadium was not identified in the decomposition products in the form of any compound by X-ray analysis.

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Bylo utaveno 12 vanadových skel s proměnlivým obsahem oxidů SiO_2 (10—70%), Al_2O_3 (16—42%) a V_1O_5 (0—33%) a konstantním obsahem Na_2O(17%). Tato skla byla alterována při teplotách 90 a 180 °C v prostředí zásaditých roztoků sodných a draselných anorg. louhů a karbonátů. Byla sledována závislost výskytu jednotlivých minerálních fází, především zeolitů, v alteračních produktech skel na proměrech obsahů oxidů Al_2O_3—SiO_2—V_2O_5 ve sklech, teplotě a na složení hydrotermálních roztoků. Oblasti vzniku minerálních fází v provedených experimentech jsou zřejmé z diagramů trojsložkové soustavy na obr. 1-7. Při vyšší teplotě (180 °C) byly produkty reakcí především živce, foidy, jílové minerály, cancrinit; ze zeolitů při této teplotě vznikal pouze analcim. Teplota 90 °C byla pro vznik zeolitů mnohem příznivější. V závislosti na sledovaných podmínkách v těchto experimentech kromě sodalitu vznikaly phlillipsit, natrolit, chabazit, analcim a syntetické zeolity P_C, A, KH a F.

Ve vzorcích vznikajících zeolitů byl sledován obsah vanadu. Nejvyšší jeho hodnoty byly nalezeny v analcimu (3—10%), nízké (1—2%) u zeolitů A a F a prakticky nulové v phillipsitu a zeolitu P_C.

Obr. 1. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálních rozkladů na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech.*

90 °C, 2 M Na_2CO_3
———— — *zeolit* P_C
—— · · · · — *sodalit*
· —— . —— *natrolit.*

Obr. 2. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálních rozkladů na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech.*

90 °C, 2M NaOH
· · ————— *zeolit* P_C
· · · · —— —— *sodalit*
◑ *zeolit A.*
▲ *chabazit.*

Obr. 3. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálních rozkladů na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech.*

90 °C, 2 M (NaOH + KOH)
— ——————— *phillipsit*
—— —— —— *chabazit*
—— . —— *zeolit KH*
—— . . —— *zeolit F.*

Obr. 4. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálncích rozkladů na obsazích Si_2O, Al_2O_3 *a* V_2O_5 *ve sklech.*

90 °C, 2 M K_2CO_3
— · ————— *phillipsit*
—— —— —— *K sodalit*
—— . . —— *leucit*
◑ *zeolit F.*

Obr. 5. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálních rozkladů na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech.*

180 °C, 2 M Na_2CO_3
————— *jílový minerál*
—— —— . . *cancrinit*
. . . . . *analcim.*

Obr. 6. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálních rozkladů na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech.*

180 °C, 2 M K_2CO_3
———————— *jílový minerál*
—— —— . . *cancrinit*
. . . . *analcim.*

Obr. 7. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálních rozkladů na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech.*

180 °C, 2 M K_2CO_3
———————— *jílový minerál*
—— —— - - - *kalsilit (trikalsilit)*
——— . ——— *leucit*
- - - . ——— *K-živec*

Obr. 8. Hydroxisodalit, Va-21 NaOH, *90 °C.*

Obr. 9. K-sodalit, Va-11, K_2CO_3, *90 °C.*

Obr. 10. Zeolit F, Va-11, NaON + KOH, *90 °C.*

Obr. 11. Phillipsite, Va-13 K_0CO_3, *90°C.*

Obr. 12. Zeolit Pcl *Va-13,* NaOH, *90 °C.*

Obr. 13. Zeolit A, Va-17, NaOH, *90 °C.*

Obr. 14. Zeolit A, Va-17, NaOH, *90 °C.*

Obr. 15. Chabazit, Va-1, NaOH + KOH, *90 °C.*

ГИДРОТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ВАНАДИЕВЫХ СТЕКОЛ

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Приготовили 12 ванадиевых стекол с изменяющимся содержанием оксидов SiO_2 (10 — 70 %), Al_2O_3 (16—42 %) и V_2O_5 (0—33 %) с постоянным содержанием Na_2O (17 %). Приводимые стекла альтернировали при температурах **90** и 180 °C в среде щелочных растворов натриевых и калиевых неорганических щелочей и карбонатов. Исследовали зависимость появления отдельных минеральных фаз, прежде всего цеолитов, в альтерационных продуктах в зависимости от изменяющихся содержаний оксидов $Al_2O_3—SiO_2—V_2O_5$ в стеклах, температуры и состава гидротермических растворов. Области образования минеральных фаз в проводимых экспериментах видны из диаграмм трехкомпонентной системы, находящихся на рис. 1—7. При более высокой температуре (180 °C) продуктами реакции явились прежде всего полевые шпаты, фоиды, илистые минералы, канкринит; из цеолитов при данной температуре образовался только анальцим. Температура 90 °C оказывается для образования цеолитов более пригодной. В зависимости от исследуемых условий в приводимых экспериментах кроме содалита образовались цеолиты, филлипсит, натролит, хабазит, анальцим и синтетические цеолиты *Pc*, *A*, *KH* и *F*.

В пробах образующихся цеолитов исследовали содержание ванадия. Его наиболее высокие величины были найдены в анальциме (3—10 %) и наиболее низкие в цеолитах *A* и *F* и практически нулевое содержание установили в филлипсите и цеолите *Pc*.

Рис. 1. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз в продуктах гидротермического разложения от содержания SiO_2, Al_2O_3 и V_2O_5 *в стеклах; 90 °C, 2 M* Ha_2CO_3, ———— цеолит *Pc*, - - - - - *содалит*, - - . - - . - - . — *натролит.*

Рис. 2. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз в продуктах гидротермических разложений от содержаний SiO_2, Al_2O_3 *и* V_2O_5 *в стеклах: 90 °C, 2 M* NaOH, ——— цеолит *Pc*, ----— содалит, ◑ *цеолит A*, ◓ *хабазит.*

Рис. 3. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз в продуктах гидротермических разложений от содержаний SiO_2, Al_2O_3 *и* V_2O_5 *в стеклах: 90 °C, 2 M* (NaOH + KOH), ——— *филлипсит*, - - - - *хабазит*, — .— .— *цеолит*, KH, — . .— *цеолит F.*

Рис. 4. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз в продуктах гидротермических разложений от содержаний SiO_2, Al_2O_3 *и* V_2O_5 *в стеклах: 90 °C, 2 M* K_2CO_3, ——— *филлипсит*, ----— K *содалит*, — . .— *леуцит*, ◑ *цеолит F.*

Рис. 5. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз гидротермических разложений от содержаний SiO_2, Al_2O_3 *и* V_2O_5 *в стеклах: 180 °C, 2 M* Na_2CO_3, ——— *илистый минерал*, —— . . *канкринит*, ... *анальцим.*

Рис. 6. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз в продуктах гидротермических разложений от содержаний SiO_2, Al_2O_3 *и* V_2O_5: *180 °C, 2 M* K_2CO_3, ——— *илистый минерал*, ---- . . *канкринит*, . . . *анальцим.*

Рис. 7. Трехкомпонентная диаграмма. Зависимость появления минеральных фаз в продуктах гидротермических разложений от содержанпйй SiO_2, Al_2O_3 *и* V_2O_5 *в стеклах: 180 °C, 2 M* K_2CO_3, ——— *илистый минерал*, ---— *калсилит (трикалсилит)*, — . .— *леуцит*, — .— *K — полевой шпат.*

Рис. 8. Гидроксисодалит, Va-21, NaOH, *90 °C.*

Рис. 9. K-*содалит*, Va-11, K_2CO_3, *90 °C.*

Рис. 10. Цеолит F, Va-11, NaOH + KOH, *90 °C.*

Рис. 11. Филлипсит, Va-13, K_2CO_3, *90 °C.*

Рис. 12. Цеолит Pc, Va-13, NaOH, *90 °C.*

Рис. 13. Цеолит A, Va-17, NaOH, *90 °C.*

Рис. 14. Цеолит A, Va-17, NaOH, *90 °C.*

Рис. 15. Хабазит, Va-1, NaOH + KOH, *90 °C.*

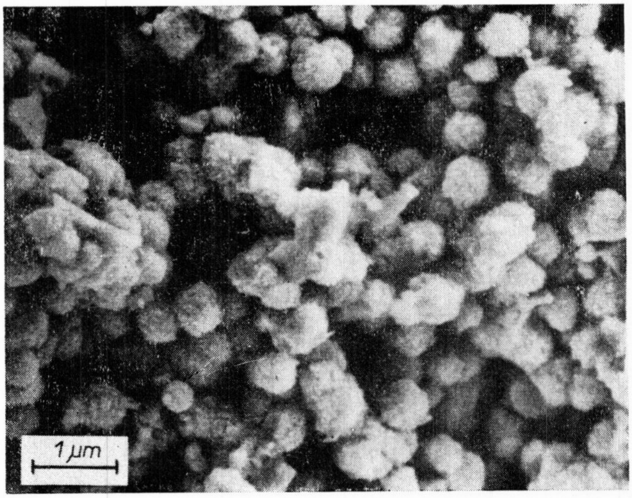

Fig. 8. Hydrosodalite, Va-21, NaOH, *90 °C.*

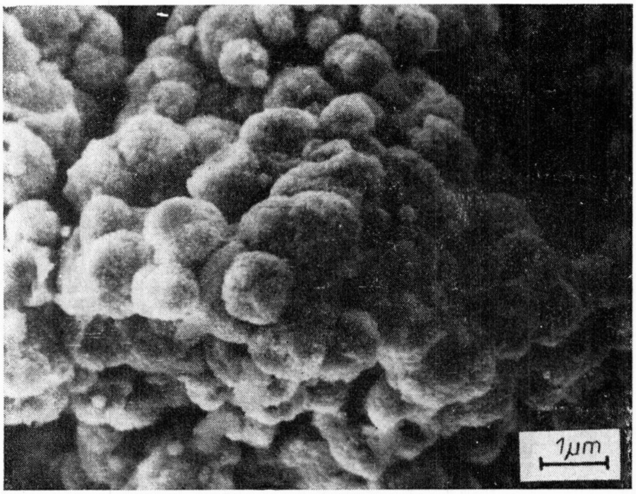

Fig. 9. K-sodalite, Va-11, K_2CO_3, *90 °C.*

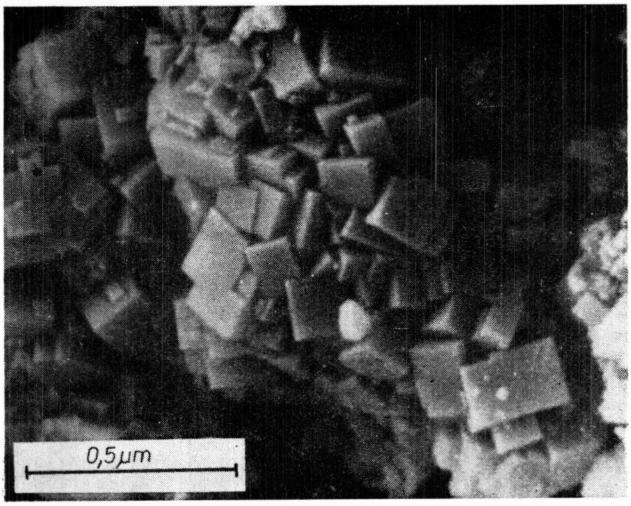

Fig. 10. Zeolite F, Va-11, NaOH + KOH, *90 °C.*

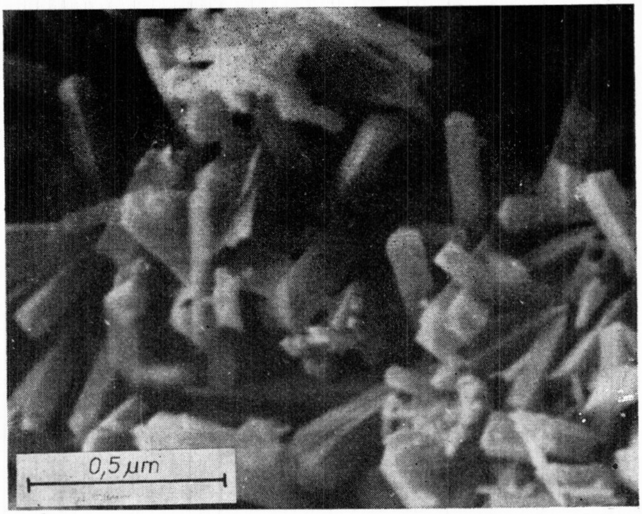

Fig. 11. Phillipsite, Va-13, $NaCO_3$, *90 °C.*

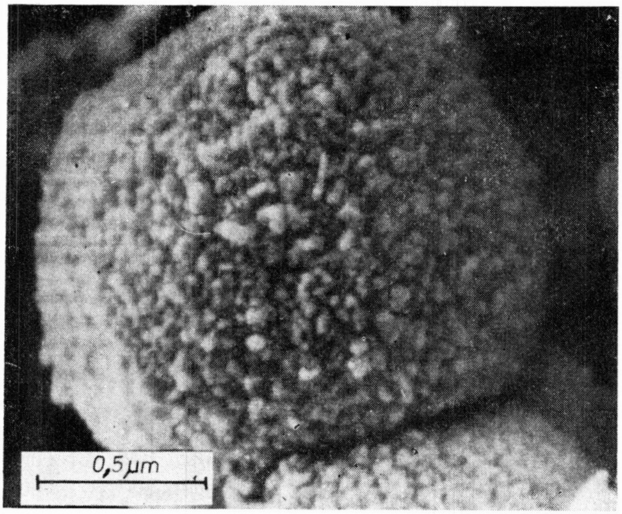

Fig. 12. Zeolite P_C*, Va-13,* NaOH, *90 °C.*

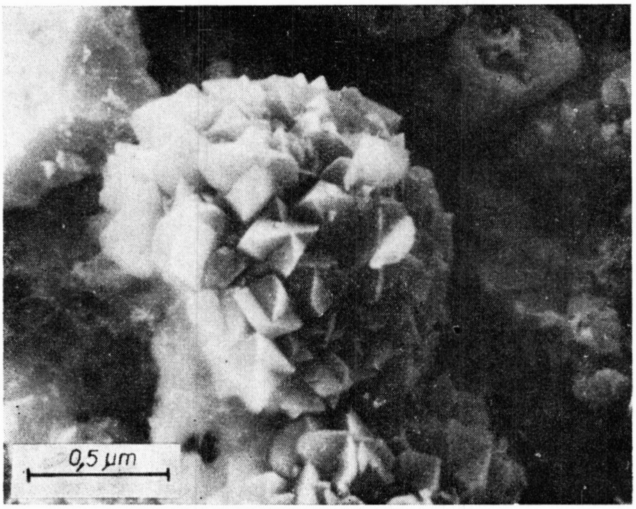

Fig. 13. Zeolite, A Va-17, NaOH, *90 °C.*

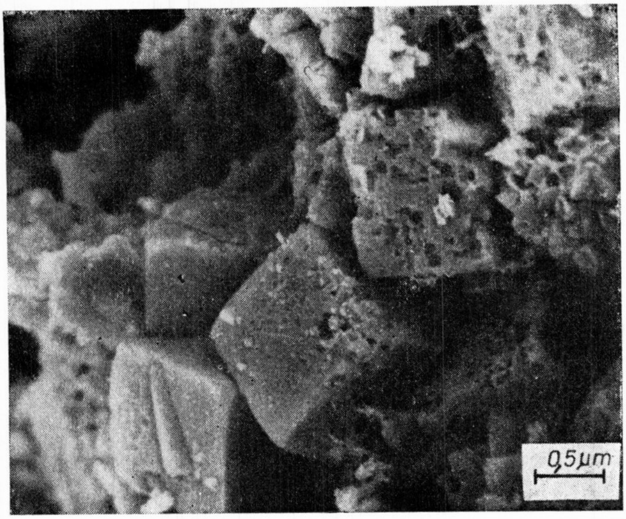

Fig. 14. Zeolite A, Va-17, NaOH, *90 °C.*

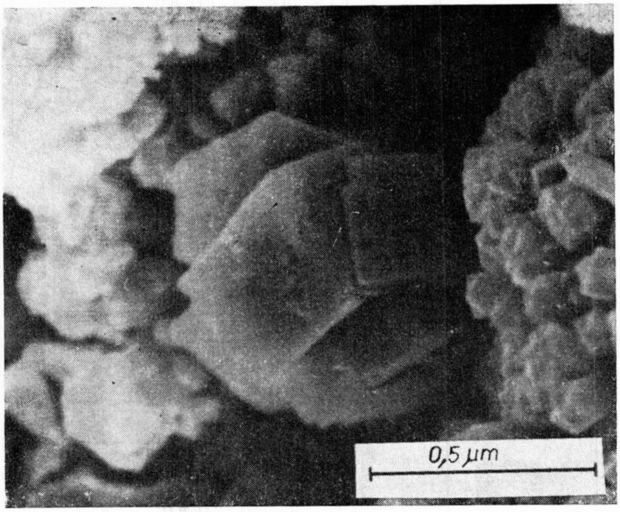

Fig. 15. Chabazite, Va-1, NaOH + KOH, *90 °C.*