HYDROTHERMAL PREPARATION OF VANADIUM ZEOLITES

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Received 24.1.1991

The study was concerned with hydrothermal alterations of synthetic vanadium glasses with a verying ratio of the oxides $SiO_2 : Al_2O_3 : V_2O_5$***, for the purpose of determining the possibility of building the vanadium atoms into the zeolitic structure. The hydrothermal decomposition of the glasses was effected in three – to eight-day cycles at 120° C in the medium of basic solutions of hydroxides or salts with a sodium or potassium cation. In this way, a series of zeolites was prepared whose properties depended on the composition of the initial glasses, in particular on their*** $SiO_2 : Al_2O_3$ ***ratio. The vanadium content in the zeolites was determined. The highest content was found in zeolite Nu-15 having the composition*** $Na_2O.Al_2O_3.3SiO_2.0.5V_2O_5$ ***(in anhydrous form). A significant content of vanadium was also found in analcime and a substantially lower one in synthetic zeolites A and KF. Zeolites of the phillipsite type contained no vanadium at all.***

INTRODUCTION

The present paper is a part of a study concerned with the possibilities of preparing vanadium zeolites by hydrothermal decomposition of glasses with a variable content of oxides – alumina, silica and vanadia, at a constant content of sodium oxide [1, 2]. Synthetic zeolites with heterogeneous metal atoms in their crystalline structure are called third-generation zeolites. At present they are subject of considerable interest as catalysts of organic as well as inorganic syntheses and oxidation-reduction reactions.

The methods used to prepare these substances so far described in the literature, were mostly based on aqueous solutions of oxides or other inorganic compounds of the initial elements (Na, Al, Si, transient metal). In most instances, the reactions yielded zeolites with a very low content of the heterogenous element, frequently absorbed in its surface.

Publications dealing with the preparation of third-generation zeolites with assumed special catalytic properties, began to be published in late sixties and early seventies [3, 4]. There were mostly patents whose authors mostly did not deal with the position of the transient metal ion in the structure of the synthetic zeolite, also for reasons of the considerable difficulty involved in such a determination. Some authors (eg. [3]) point out that with respect to the catalytical effects of these zeolites it is not important whether the heterogeneous atoms substitute aluminium or silicon atoms in the skeleton, or whether they are built into the cationic or interstitial positions. The argument is that the same catalytic effect in oxidation-reduction reactions is also exhibited by zeolites with which the heterogeneous atom in the form of some inorganic salt is sorbed in the zeolite surface. However, in that case one can nevertheless expect reduced catalytic efficiency resulting from an imperfect dispersion of the element throughout the volume of the zeolite.

Other authors [5] point out that in the case of acidobasically catalyzed reactions, the active centres are only formed by those atoms of the transient metal which are built into the zeolite structure in the position of silicon atoms. Oxidation-reduction reactions of course require the presence of ions existing in more than one valency. Such reactions therefore utilize as catalysts zeolites enriched with a transient metal either by impregnation (sorption in the zeolite surface) or by ion exchange [6, 7, 8, 9]. More recently, experiments have been carried out with building the metal into the zeolite structure by adding the oxide or an inorganic salt of the given element either into the reaction mixture [10, 11, 12, 13] or by melting the zeolite with compounds of the transient metal [14, 15].

EXPERIMENTAL

Vanadium glasses were prepared by melting mixtures of the calculated amounts of raw materials, alumina (chromatography grade, REANAL Budapest), silica (high-purity synthetic crystal), ammonium vanadate NH_4VO_5 A.R., at varying proportions (Table I) with a constant amount of Na_2CO_3 A.R. (LACHEMA Brno) as flux. The glasses were ground to analytical fineness (200 mesh) and decomposed hydrothermally in the medium of 2M solutions of sodium and potassium carbonate and sodium hydroxide at 120°C and under saturated vapour pressure (approx. 78% autoclave charging) in steel autoclaves whose design was described in [16]. To rule out contamination of the reaction mixture with iron from the autoclave walls, the aqueous suspensions of samples were placed in titanium cartridges of about 6.5 ml capacity. The experiments were carried out at three- to eight-day intervals.

The products of decomposition were removed from the autoclave and decanted several times with dilute hydrochloric acid and 2M sodium perchlorate in order to eliminate V_2O_5 which may have absorbed

Table I

Chemical composition of the glasses. Comparison of the calculated values of the content of oxides with the analytical values

Glass	Na_2O [wt.%]		Al_2O_3 [wt.%]		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	24.95	60.3	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
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	14.5	8.43	31.2	32.32	100

in the surface of the mineral phases, then with distilled water, and then dried at room temperature.

The mineral phases of the decomposition products were identified by X-ray analysis (diffractograph Chirana, CuK_α radiation, Ni filter) and by microscopy (JOEL JXA-50A electron microprobe). The X-ray patterns were evaluated by means of powder diffraction data, as well as by means of a database of interplanar distances and intensities for synthetic zeolites.

The secondary electron method (SEI) was used to determine the morphology of zeolitic crystals by means of the electron microprobe, at 600 to 5000 magnification (Figs. 7 through 14). The results were compared with the micrographs of crystals in the literature [17, 18]. The method was likewise utilized for estimating the degree of conversion of the glasses, and the well identifiable zeolite crystals were analyzed for their Na, K, Al, Si and V content by means of the EDAX microprobe accessories.

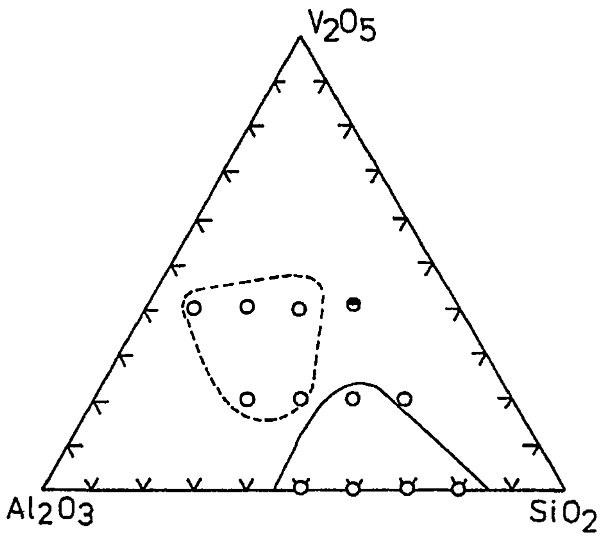

Fig. 1. Three-component diagram. Occurrence of mineral phases in products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses. 120° C,* 2M Na_2CO_3, *3 days..*
——— *synthetic phillipsite* (P_c),
— — — *sodalite,* ● *analcime.*

RESULTS AND DISCUSSION

The mineral phases identified in the products of hydrothermal decomposition of vanadium glasses are listed in Table II and plotted in the diagrams of the $Al_2O_3 - SiO_2 - V_2O_5$ three-component system (calculated values of content in glasses free of Na_2O – cf. Table III). These diagrams, expressing the regions of occurrence of the individual mineral phases in the decomposition products in terms of composition of the original vanadium glasses, are shown in Figs. 1 through 6. The curves demarcate the crystallization fields of zeolitic minerals formed in the system $Na_2O - SiO_2 - Al_2O_3 - V_2O_5 - H_2O$ under the given conditions of the hydrothermal process and cannot be regarded as regions of their kinetic stability (not

Table II

Products of alteration of the vanadium glasses at 120°C

Glass	Time [days]	Medium of		
		2M Na_2CO_3	2M K_2CO_3	2M NaOH
Va-1	3	zeol. P_c	calsilite, phillipsite	zeol. P_c, cancrinite
	8	analcime	phillipsite, sanidine	analcime, faujasite
Va-3	3	davyne, hyalophane	phillipsite, orthoclase	nepheline, kaolin
	8	analcime, cancrinite	phillipsite, sanidine	zeol. P_c, analcime
Va-5	3	analcime	phillipsite, zeol. KH	analcime
	8	analcime	phillipsite, zeol. KH	zeol. Nu-15
Va-7	3	zeol. P_c	phillipsite	zeol. P_c, nepheline
	8	analcime	phillipsite,zeol. KH	analcime
Va-9	3	zeol. P_c	phillipsite, zeol. KH	faujasite, zeol. P_c
	8	analcime	phillipsite, cristobalite	zeol. P_c, faujasite
Va-11	3	sodalite	K-sodalite, zeol. KH	zeol. A, sodalite
	8	sodalite	K-sodalite, cristobalite	hydroxysodalite
Va-13	3	zeol. P_c	nepheline	zeol. P_c
	8	zeol. P_c	zeol. A	zeol. P_c
Va-15	3	sodalite, cristobalite	tricalsilite, nepheline	zeol. A,zeol. P_c
	8	sodalite, analcime	zeol. A, phillipsite	zeol. A,zeol. P_c
Va-17	3	sodalite, cristobalite	K-sodalite	zeol. A, hydroxysodalite
	8	sodalite, zeol. P_c	K-sodalite	zeol. P_c, hydroxysodalite
Va-19	3	zeol. P_c	K-sodalite, cristobalite	zeol. P_c
	8	zeol. P_c	K-sodalite, zeol. A	zeol. P_c
Va-21	3	sodalite	K-sodalite	hydroxysodalite
	8	sodalite	K-sodalite	hydroxysodalite
Va-23	3	sodalite	K-sodalite	hydroxysodalite
	8	sodalite	zeol. KF, nepheline	hydroxysodalite

enough experimental data available for this purpose).

A) In the medium of 2M solution of Na_2CO_3, the products of hydrothermal decomposition of the glasses contained most often analcime, sodium phillipsite (designated also as synthetic zeolite P_c in the literature[1]) and sodalite. These phases were formed either as monomineral alteration products (partial or total) or occurred jointly as two products, in dependence on the composition of the initial glasses, as follows from the diagrams in Figs. 1 and 2.

The dependence of the type of the arising minerals on the composition of the glasses is obvious particularly with zeolite P_c and sodalite. Zeolite P_c was formed in the regions of higher SiO_2 content and a low or zero content of V_2O_5. On the other hand, the regions with higher SiO_2 (and lower Al_2O_3) in the presence of V_2O_5 in the glass yielded first of all so-

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[1] Unlike natural phillipsite which is a sodium-potassium hydrated aluminosilicate, the zeolite called in the literature synthetic phillipsite or zeolite P_c, which is formed only in the presence of sodium cations, does not contain any potassium.

Table III

Calculated content of Al_2O_3, SiO_2 and V_2O_5 in the glasses (wt. %) (the content of Na_2O is not included)

Glass	Al_2O_3	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

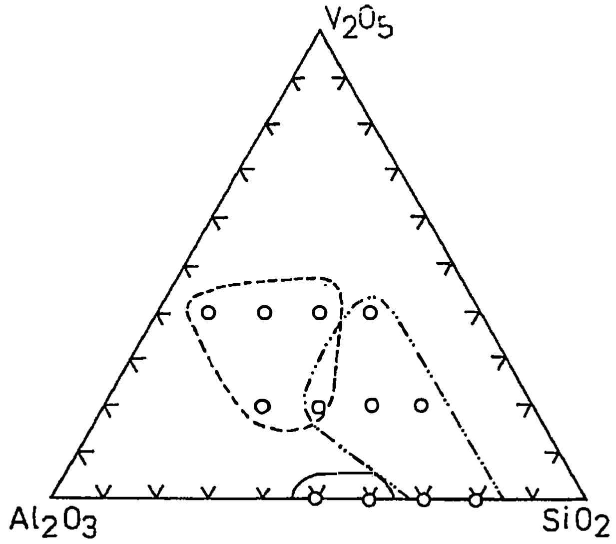

Fig. 2. Three-component diagram. Occurrence of mineral phases in products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses. 120°C,* 2M Na_2CO_3, *8 days.*

———————— *synthetic phillipsite* (P_c),

—— —— —— *sodalite,*

——··——··—— *analcime.*

dalite, as also corresponds to the composition of the two minerals. The effect of the length of hydrothermal decomposition was that the synthetic phillipsite tended to be raplaced with analcime which, as also indicated by other authors [19], is the most stable mineral phase of the products yielded by long-term hydrothermal decomposition.

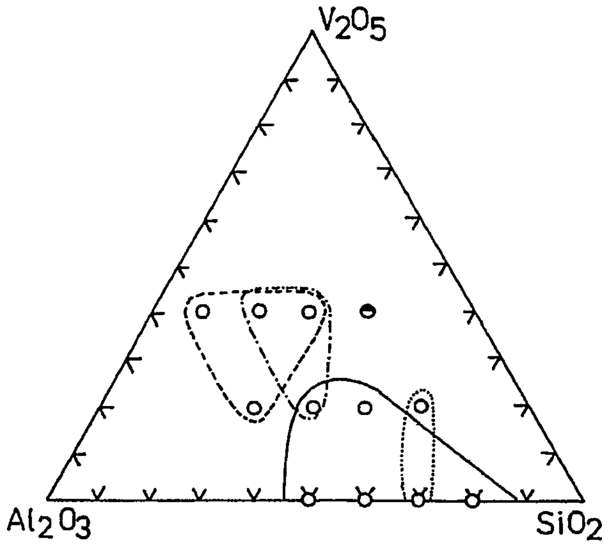

Fig. 3. Three-component diagram. Occurence of mineral phases in products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses. 120°C,* 2M NaOH, *3 days.*

———————— *synthetic phillipsite* (P_c),

—— —— —— *sodalite,* ⊖ *analcime,*

——·——·—— *zeolite A,*

· · · · · · *nepheline.*

B) In the medium of 2M NaOH solution, the relationships with respect to zeolite P_c and sodalite were similar to those of the Na_2CO_3 medium. In addition to these minerals, there was also an additional product, zeolite A, in the region of medium to lower SiO_2 content in the glasses (Figs. 3 and 4); faujasite and nepheline were also found as by-products in separate cases. In this medium, analcime formed in the three-day cycle by decomposition of glass designated Va-5 and having the highest V_2O_5 content, and after the 8-day exposure was replaced by vanadium zeolite Nu-15. Similarly to the Na_2CO_3 medium, even in this case longer hydrothermal decomposition (8 days) resulted in the formation of analcime instead of phillipsite and nepheline. The crystallization field of the sodalite phase in the products of decomposition remained unchanged.

For both sodium decomposition media over the respective temperature range, the dependence of the formation of mineral phases on the increasing ratio of $SiO_2 : Al_2O_3$ in the glasses can be expressed as the series sodalite (hydroxysodalite) – zeolite A (only in NaOH) – synthetic phillipsite + faujasite – NU-15 (only in NAOH) – analcime.

C) In the medium of 2M K_2CO_3, the main products of hydrothermal decomposition of the glasses were again phillipsite and sodalite (Figs. 5 and 6). However, in contrast to the sodium media, the phas-

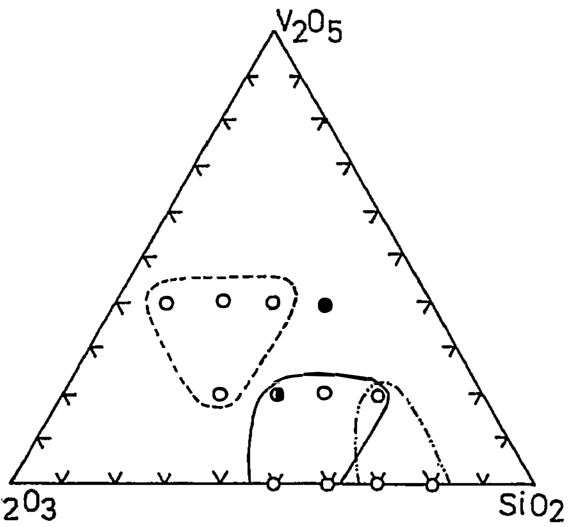

Fig. 4. Three-component diagram. Occurrence of mineral phases in products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses. 120° C,* 2M NaOH, *8 days.*

——————— *synthetic phillipsite* (P_c),
—— —— —— *sodalite,*
——··——··—— *analcime,*
◑ *zeolite A,* ● *zeolite Nu-15.*

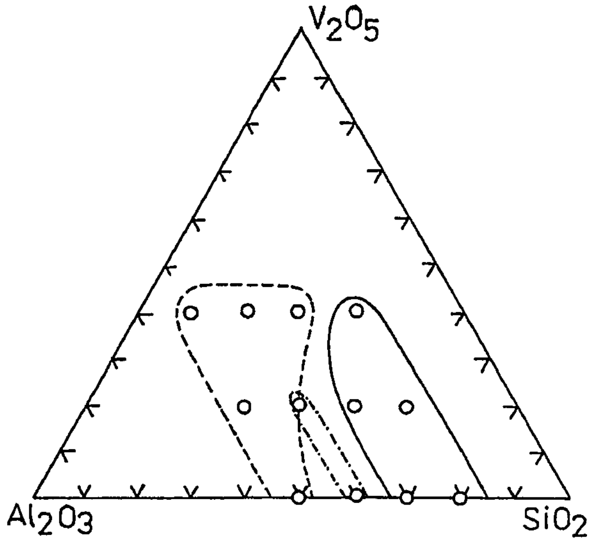

Fig. 5. Three-component diagram. Occurrence of mineral phases in products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses. 120° C,* 2M K_2CO_3, *8 days.*

——————— *phillipsite,*
—— —— —— Na–K *sodalite,*
——·——·—— *nepheline.*

es contained both sodium and potassium cations, as proved by the EDAX analyses (Table IV). Zeolite KH, zeolite A, potassium feldspars and feldspar representative calsilite, tricalsilite and nepheline, and exceptionally also cristobalite were also found as minority products of the hydrothermal alterations. The degree of hydrothermal decomposition of glasses was the lowest in the potassium medium : microscopic examinations showed that most of the specimens were decomposed to less than 50%.

The relationship between the formation of the main mineral phases and the composition of the initial glasses was the same as with the medium of sodium solutions. Nepheline was formed from glasses with a medium content of SiO_2 (at a $SiO_2 : Al_2O_3$ ratio of 1 – 1.5) and with a lower or zero content of V_2O_5. After longer hydrothermal treatment, nepheline was converted to zeolite A. Potassium feldspars were found as by-products of phillipsite following decomposition of glasses with high SiO_2 contents. The KH synthetic zeolite was likewise a by-product of phillipsite, mostly with glasses with a higher V_2O_5 content ($SiO_2 : Al_2O_3$ about 2). It is therefore possible that in this case, vanadium acts as a catalyst of reactions producing zeolite KH.

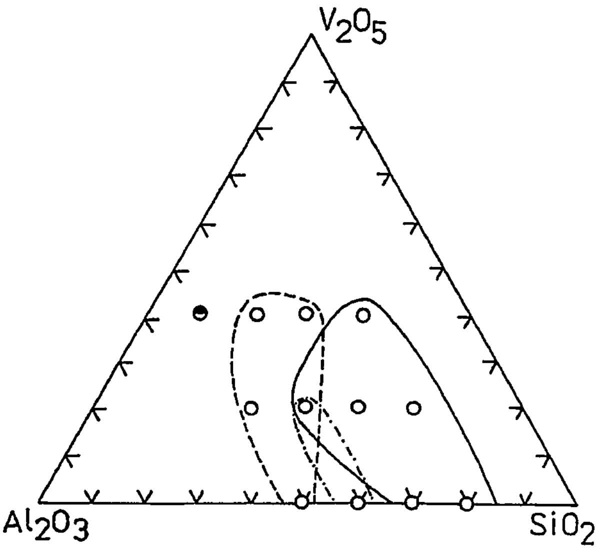

Fig. 6. Three-component diagram. Occurrence of mineral phases in products of hydrothermal decomposition vs. the content of SiO_2, Al_2O_3 *and* V_2O_5 *in the glasses. 120° C,* 2M K_2CO_3, *8 days.*

——————— *phillipsite,*
—— —— —— Na–K *sodalite,*
——·——·—— *zeolite A,* ● *zeolite KF.*

The content of vanadium in the individual mineral phases was determined from semiquantitative chemical analyses of the reaction products, carried out by the EDAX microprobe method. The analyses showed that vanadium is virtually not present in

Table IV

Chemical analyses (EDAX) of mineral phases in the products of hydrothermal alteration of vanadium glasses

Mineral	Conditions of decomposition	Content of element in mineral [%]				
		Na	K	Al	Si	V
sodalite	Va-11, Na_2CO_3, 8 days	17	-	33	48	2
	Va-15, Na_2CO_3, 3 days	19	-	36	43	2
	VA-15, Na_2CO_3, 8 days	17	-	31	44	8
	Va-17, Na_2CO_3, 8 days	17	-	28	45	10
	Va-21, Na_2CO_3, 8 days	17	-	33	47	3
hydroxy-sodalite	Va-17, NaOH, 8 days	13	-	32	46	9
	Va-17, NaOH, 3 days	16	-	33	47	4
	Va-11, NaOH, 8 days	17	-	33	47	3
	Va-21, NaOH, 8 days	18	-	32	45	5
	Va-23, NaOH, 8 days	19	-	37	41	3
Na-K sodalite	Va-21, K_2CO_3, 3 days	9	19	27	41	4
zeolite P_c	Va-5, NaOH, 3 days	21	-	24	54	<1
	Va-9, NaOH, 8 days	17	-	32	51	<1
	Va-15, NaOH, 3 days	17	-	31	61	<1
	Va-15, NaOH, 8 days	16	-	33	51	<1
phillipsite	Va-3, K_2CO_3, 8 days	13	15	27	45	<1
	Va-9, K_2CO_3, 8 days	12	14	28	44	<1
	Va-9, K_2CO_3, 8 days	8	16	27	49	<1
analcime	Va-3, Na_2CO_3, 8 days	13	-	16	58	10
	Va-5, Na_2CO_3, 3 days	13	-	21	63	3
	Va-9, Na_2CO_3, 8 days	15	-	27	51	7
zeolite KF	Va-23, K_2CO_3, 8 days	13	29	40	16	2
zeolite A	Va-15, NaOH, 3 days	26	-	31	42	1
	Va-15, NaOH, 8 days	21	-	32	45	1 – 2
zeolite Nu-15	Va-5, NaOH, 8 days	15	-	19	46	20

any of the phillipsite types (tenths of percent only). On the average, about 1% of vanadium was determined in zeolite A, roughly 2% in zeolite KF. A high vanadium content was established in all types of sodalite (2 – 14%) and in analcime (3 – 10%). The highest vanadium content was found in the product of 8-day hydrothermal treatment (17 – 23%) of glass designated Va-5, in the medium of 2M NaOH solution. The diffraction pattern of the product was very similar to that of vanadium zeolite Nu-10 (13). The values of interplanar distances and intensities of the two substances are listed in Table V. In view of the different chemical composition (particularly a higher V_2O_5 content), the specimen was designated Nu-15 [20]. The results of 36 analyses of this mineral, carried out with the electron microprobe, were used to determine its formula (without the crystalline water which the method does not allow to be determined), namely as $Na_2O.Al_2O_3.3SiO_2.0.5V_2O_5$. The formula should be regarded as an approximate one with respect to the accuracy of the analytical method employed. The yield of the Nu-15 zeolite under the given conditions was 100%. Even though the position taken by the vanadium atoms could not be established

Table V

Values of interplanar distances *d* and their relative intensities *I* for zeolites Nu-10 and Nu-15

Nu-10		Nu-15	
d	*I*	*d*	*I*
10.95	m→s	10.40	60
8.80	w→m	8.27	40
6.99	w→m	6.42	40
5.41	w	5.54	25
4.57	wm		
4.38	vs	4.41	100
3.69	vs	3.69	65
3.63	vs	3.60	70
3.48	m→s	3.41	90
3.36	w	3.26	90
3.31	w		
2.78	w	2.76	45
2.53	m	2.54	5
2.44	w	2.44	5
2.37	w	2.36	5
1.88	w	1.89	10

within the framework of the present study, the vanadium should obviously not be absorbed in the zeolite surface, as in that case it would be removed by the multiple decantation with HCl and $NaClO_4$. The vanadium was likewise not identified in the form of any of its compound by X-ray analysis in the products of hydrothermal decomposition.

CONCLUSION

Hydrothermal decomposition of vanadium glasses yielded a number of zeolites whose occurrence in the decomposition products depended on the composition of the initial glasses, the medium and the duration of the hydrothermal process.

In the medium of Na_2CO_3 and NaOH solutions, phillipsite was for the most part the main product of shorter hydrothermal treatment, and tended to convert to analcime on prolonged hydrothermal decomposition.

In terms of increasing $SiO_2 : Al_2O_3$ ratio in the initial glasses, the occurrence of zeolites in the products of hydrothermal decomposition can be generally expressed by the following sequences:

- in sodium medium (Na_2CO_3, NaOH):
  zeolite A – synth. phillipsite – faujasite – Nu-15 – analcime
- in potassium medium (K_2CO_3):
  zeolite A – phillipsite – zeolite KH – phillipsite.

In separate cases and smaller amounts, also other zeolites such as natrolite and chabazite were found in the products of decomposition of vanadium glasses.

The highest vanadium content (on the average 20%) was determined analytically in the new Nu-15 zeolite (the formula of its anhydrous form being $Na_2O.Al_2O_3.3SiO_2.0.5V_2O_5$).

Quite high vanadium concentrations (3 – 10%) were also found in analcime. About 1 – 2% of this element were determined in zeolites A and KF. No vanadium was found in soda-potash phillipsite nor soda phillipsite (P_c).

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HYDROTERMÁLNÍ PŘÍPRAVA VANADIČNÝCH ZEOLITŮ

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12 syntetických vanadových skel s obsahem 10 – 17% SiO_2, 16 – 42% Al_2O_3, 0 – 33% V_2O_5 a 17% Na_2O, s předem určeným poměrem těchto složek bylo hydrotermálně alternováno při teplotě 120°C v prostředí 2M roztoků NaOH, Na_2CO_3 a K_2CO_3. Rentgendifrakční mikroskopickou analýzou byly sledovány zeolity a to jednak z hlediska závislosti vzniku jednotlivých typů těchto minerálů na složení skel při daných hydrotermálních podmínkách, jednak z hlediska obsahu vanadu v nich.

Krystalizační pole hlavních minerálních fází vznikajících ze skel v prováděných experimentech jsou zřejmé z diagramů trojsložkové soustavy na obr. 1 – 6. Kromě často se vyskytujícího minerálu sodalitu byly produkty reakcí zeolity, především phillipsit a syntetický phillipsit (P_c), analcim, zeolity KH, KF a A, ojediněle a jako vedlejší produkty alterací faujasit, natrolit a chabazit. Sledovaný obsah vanadu se v zeolitech A a KF pohyboval od 1 – 2%, v analcimu dosahoval 10% (v průměru 7%). V phillipsitu ani zeolitu P_c nebyl vanad obsažen vůbec. Nejvyšší jeho obsah (17 – 23%) byl nalezen v zeolitu Nu-15, jehož vzorec v bezvodé formě byl určen jako $Na_2O.Al_2O_3.3SiO_2.0,5V_2O_5$.

Obr. 1. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálního rozkladu na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech. 120°C,* 2M Na_2CO_3, *3 dny;*
———— *synt. phillipsit* (*P_c*);
— — — *sodalit;* ⊖ *analcim.*

Obr. 2. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálního rozkladu na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech. 120°C,* 2M Na_2CO_3, *8 dní.*
———— *synt. phillipsit* (*P_c*);
— — — *sodalit;*
——··——··—— *analcim.*

Obr. 3. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálního rozkladu na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech. 120°C,* 2M NaOH, *3 dny.*
———— *synt. phillipsit* (*P_c*);
— — — *sodalit;* ⊖ *analcim;*
——·——·—— *zeolit A;* · · · · · *nephelin.*

Obr. 4. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálního rozkladu na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech. 120°C,* 2M NaOH, *8 dní.*
———— *synt. phillipsit* (*P_c*);
— — — *sodalit;*
——··——··—— *analcim;*
◑ *zeolit A;* ● *zeolit Nu-15.*

Obr. 5. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálního rozkladu na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech. 120°C,* 2M K_2CO_3, *3 dny.*
———— *phillipsit;*
— — — Na–K *sodalit;*
——·——·—— *nephelin.*

Obr. 6. Trojsložkový diagram. Závislost výskytu minerálních fází v produktech hydrotermálního rozkladu na obsazích SiO_2, Al_2O_3 *a* V_2O_5 *ve sklech. 120°C,* 2M K_2CO_3, *8 dní.*
———— *phillipsit;*
— — — Na–K *sodalit;*
——·——·—— *zeolit A;* ⊖ *zeolit KF.*

Obr. 7. Hydroxysodalit, Va-11, 2 M NaOH, *3 dny.*

Obr. 8. Na–K *sodalit,* Va-17, 2 M K_2CO_3, *3 dny.*

Obr. 9. Analcim, Va-7, 2 M NaOH, *8 dní.*

Obr. 10. Zeolit A, Va-15, 2 M NaOH, *8 dní.*

Obr. 11. Phillipsit, Va-1, 2 M K_2CO_3, *8 dní.*

Obr. 12. Synt. phillipsit P_c, Va-13, 2 M NaOH, *8 dní.*

Obr. 13. Synt. phyllipsit P_c, Va-13, 2 M Na_2CO_3, *8 dní.*

Obr. 14. Zeolit Nu-15, Va-5, 2 M NaOH, *8 dní.*

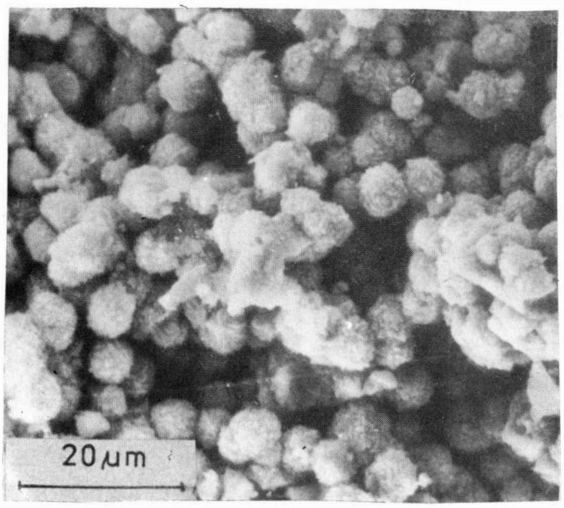

Fig. 7. Hydroxysodalite, Va-11, 2M $NaOH$, *3 days.*

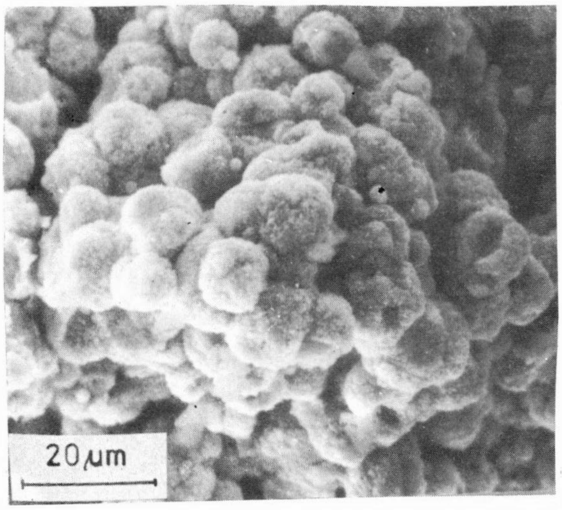

Fig. 8. Na-K sodalite, Va-17, 2M K_2CO_3, *3 days.*

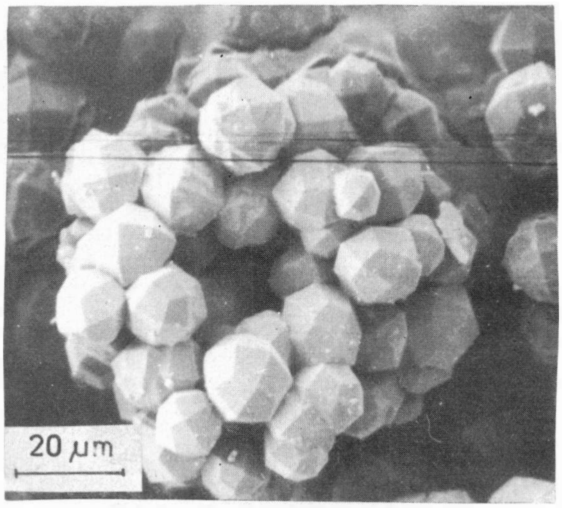

Fig. 9. Analcime, Va-7, 2M $NaOH$, *8 days.*

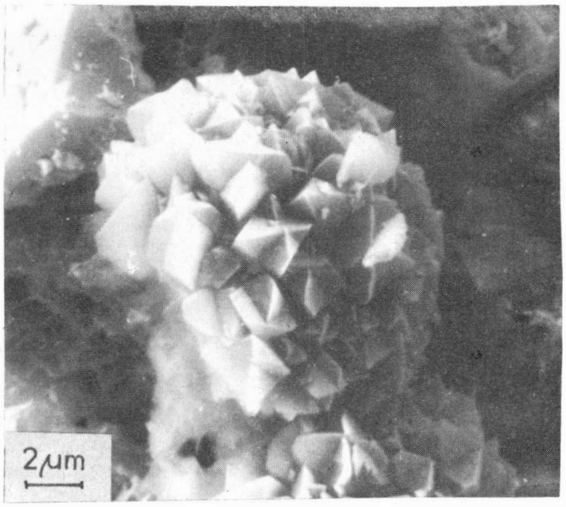

Fig. 10. Zeolite A, Va-15, 2M $NaOH$, *8 days.*

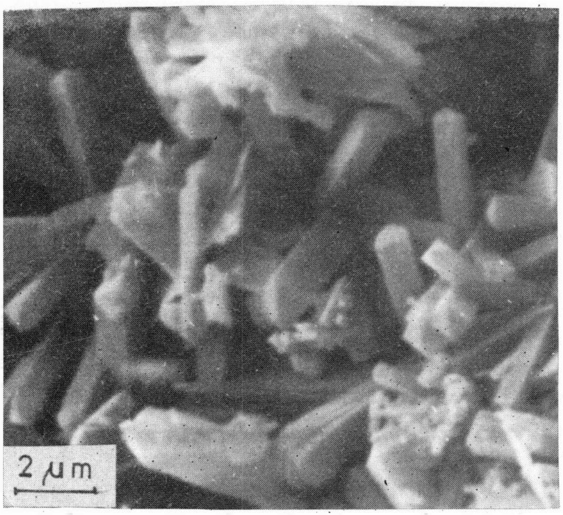

Fig. 11. Phillipsite, Va-1, 2M K_2CO_3, *8 days.*

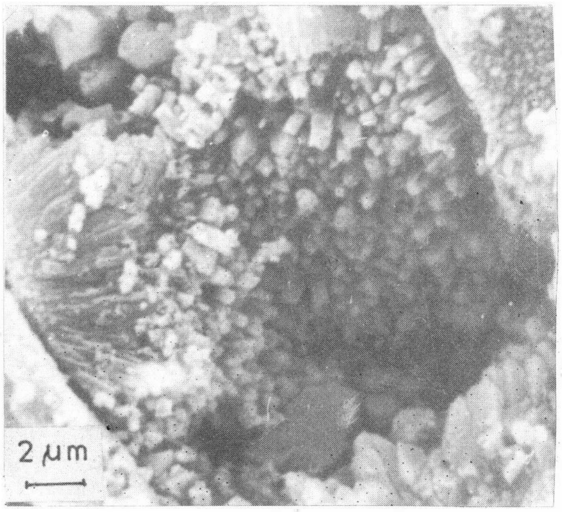

Fig. 13. Synthetic phillipsite P_c, Va-13, 2M Na_2CO_3, *8 days.*

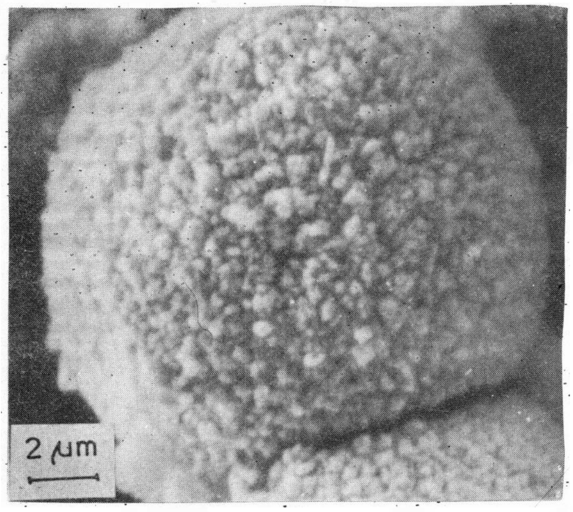

Fig. 12. Synthetic phillipsite P_c, Va-13, 2M NaOH, *8 days.*

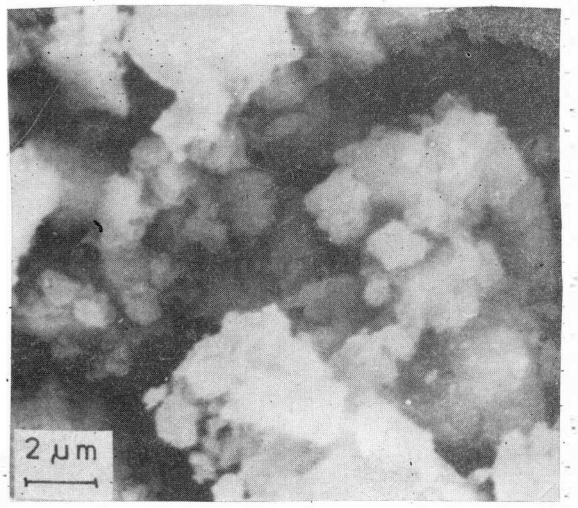

Fig. 14. Zeolite Nu-15, Va-5, 2M NaOH, *8 days.*