

## PREPARATION OF THE ZEOLITE Nu-15

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Received November 8, 1989

Accepted January 9, 1990

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A new vanadium zeolite labelled Nu-15 was prepared. The preparation procedure consists in hydrothermal decomposition of a vanadium glass for 4–10 days at 120–160°C and saturated vapour pressure in a strongly basic solution of sodium hydroxide. The composition of the starting glasses was 15–17% Na<sub>2</sub>O, 15–17% Al<sub>2</sub>O<sub>3</sub>, 25–40% SiO<sub>2</sub> and 30–45% V<sub>2</sub>O<sub>5</sub>, the composition of the zeolite, apart from water, corresponds to the formula 2 Na<sub>2</sub>O·2 Al<sub>2</sub>O<sub>3</sub>·6 SiO<sub>2</sub>·V<sub>2</sub>O<sub>5</sub>.

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The synthesis of the zeolite Nu-15 is the outcome of a more extensive work<sup>1</sup> which included hydrothermal decomposition of glasses with variable Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> contents at a constant Na<sub>2</sub>O content with the aim to examine the possibility of preparing vanadium zeolites in this manner. Synthetic zeolites containing heterogeneous atoms of transition elements in their crystal lattices, referred to as zeolites of the third generation, are attracting interest as promising catalysts.

So far, attempts at the preparation of vanadium zeolites started largely from aqueous solutions or sols of oxides or other inorganic compounds of the basic elements (Al, Si, Na, V). Zeolites with low vanadium contents, with this element often sorbed on the surface, mostly emerged.

Papers dealing with the preparation of zeolites of the third generation at a general level began to appear in the late 1960's and early 1970's (refs<sup>2,3</sup>). Literature pertaining to this problem was mostly patent-oriented. The authors largely avoided the intricate problem of the positions the transition element atoms occupy in the zeolite structure; as a matter of fact, as pointed out by Levina and coworkers<sup>2</sup>, it is not decisive for the catalytic effect of the zeolites whether the heterogeneous atoms substitute Al or Si atoms in the lattice or whether they are incorporated in the cationic positions or structure cavities. These authors also claim that zeolites where the atoms of the heterogeneous element, in the form of an inorganic salt, are sorbed on the zeolite surface, exhibit the same catalytic effect in oxidation-reduction reactions. Nevertheless, in this case the catalytic efficiency is surely lower because of the imperfect distribution of the element across the zeolite bulk.

According to Habersberger and coworkers<sup>4</sup>, only the metal incorporated in the zeolite lattice in the Si positions forms active centres for acid-base catalyzed reactions

such as dehydration of methanol to hydrocarbons. For oxidation-reduction reactions, on the other hand, only the presence of an ion that can occur in more than one valency as Al and Si is prerequisite. For such reactions, zeolites enriched with the transition metal either by impregnation (sorption on the catalyst surface) or by ion exchange<sup>5-7</sup> are employed as catalysts. Attempts to incorporate the metal into the crystal lattice of the zeolite have also been made recently; two types of procedure for this preparation are used: 1) fusion of the zeolite with compounds of transition elements, and 2) preparation from gels or sols of oxides or other inorganic compounds of the basic elements.

The former approach has been applied by Kucherov and Slinkina<sup>8</sup> and by Mukhlerov and coworkers<sup>9</sup>, the latter has been used by a number of authors, some of the work, however, failed. Whitham<sup>10,11</sup> describes the preparation of zeolites referred to as Nu-4 and Nu-13 from oxides; he tried Fe, Cr, V, Mo, As, Sb, Mn, Ga and B as the heterogeneous elements. Wolf and coworkers<sup>12</sup> synthesized an A type zeolite in the presence of vanadium salts; the vanadium content of the aluminosilicates obtained has not been reported. Marosi and coworkers<sup>13</sup> prepared a ZSM zeolite containing 1.8% V<sub>2</sub>O<sub>3</sub> from an aqueous solution of inorganic salts. Vaughan<sup>14</sup> prepared the synthetic zeolite VK-2 by stirring the reaction mixture at 100°C. The preparation of the zeolite Nu-10 with the general formula 0.5–1.5 R<sub>2</sub>O.Y<sub>2</sub>O<sub>3</sub>.20 XO<sub>2</sub>.0–4 000 H<sub>2</sub>O, where R is a univalent cation or 1/n of a cation of valency *n*, X is Si or Ge and Y is Al, Fe, Cr, V, Mo, As, Sb, Mn, Ga or B, has been patented by Lowe and Araya<sup>15</sup>. Attempts at the incorporation of vanadium into zeolites of the ZSM type during their preparation were not very successful<sup>4,16,17</sup>. Habersberger and coworkers<sup>18</sup> were able to demonstrate that vanadium atoms are at least partly incorporated in the crystal lattice of zeolites of this type.

## EXPERIMENTAL

Vanadium glasses prepared at the Glass Research Institute in Hradec Králové were used as the starting material. Starting mixtures for the preparation of the glasses were made up from Al<sub>2</sub>O<sub>3</sub> of chromatographic grade (Reanal, Budapest), SiO<sub>2</sub> (high purity synthetic crystal), and NH<sub>4</sub>VO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> of reagent grade purity in well-defined proportions such that the mass fractions of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> in the glasses were changed in 10% steps while keeping the Na<sub>2</sub>O content constant. The mixtures were fused to obtain glass bricks of equal mass. As the V<sub>2</sub>O<sub>5</sub> content was increased, the appearance changed from light-green transparent to brown to black opaque glass. The bricks were crushed and ground to analytical size and quantitatively analyzed for Al, Si, Na and V on the EDAX facility of a JXA-50A electron microprobe (JEOL). The amorphous structure of the glass was proved by X-ray diffraction measurements.

The glasses ground to grain size below 0.057 mm were hydrothermally altered in steel autoclaves about 20 ml volume whose design has been reported<sup>19</sup>. The samples were accommodated in titanium cartridges about 6.5 ml volume in order to prevent the reaction mixture from contamination by iron from the autoclave walls. The autoclaves were heated in the vertical position in tube furnaces whose inner parts were perfectly thermally insulated to eliminate temperature gradient between the bottom and the closure of the autoclave.

The experiments were conducted at 90–180°C and at the equilibrium saturated vapour pressure (about 78% autoclave filling) for 3–8 days. Aqueous solutions of NaOH, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were tested as the reaction medium. Only those experiments leading to the vanadium zeolite Nu-15 are reported in this paper; a complete survey of the results of all experiments performed is presented in ref.<sup>1</sup>.

The decomposition products from the autoclaves were multiply decanted with dilute HCl and 2M-NaClO<sub>4</sub> for excluding vanadium sorbed on the surface, further decanted with distilled water and dried at ambient temperature. The mineral phases in the products were identified by X-ray diffraction examination on a Diffractograph instrument (Chirana) using CuK<sub>α</sub> radiation and a Ni filter, and microscopically with the JXA-50A electron microprobe; the EDAX facility of this microprobe was used for chemical analysis of the identified minerals. Jadeite served as standard for this quantitation.

In experiments where the glasses were found to have undergone extensive transformations, aluminium, silicon and vanadium in the residual solutions were also determined by conventional methods of chemical analysis.

## RESULTS

The vanadium zeolite labelled Nu-15 was obtained by decomposing glasses containing 15–17% Na<sub>2</sub>O, 15–17% Al<sub>2</sub>O<sub>3</sub>, 25–40% SiO<sub>2</sub> and 30–45% V<sub>2</sub>O<sub>5</sub> for 4–8 days at 120–160°C in a strongly basic solution of NaOH (1–4 mol l<sup>-1</sup>). The Na<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> contents of the glasses whose decomposition resulted in the formation of the zeolite Nu-15 are given in Table I; both the values calculated from the amounts of oxides added and those determined analytically are tabulated.

The X-ray diffraction patterns of the product of hydrothermal decomposition of the glasses in the above conditions resemble closely those of the vanadium zeolite Nu-10, patented by Lowe and Araya<sup>15</sup>. The interplanar distances and the relative X-ray diffraction intensities for the two synthetic minerals are given in Table II.

TABLE I  
Chemical composition of glasses (%)

Component	Glass			
	Va-5		Va-6	
	calculated	found	calculated	found
Na <sub>2</sub> O	17.08	16.0	17.0	16.3
SiO <sub>2</sub>	33.74	37.5	23.50	24.8
Al <sub>2</sub> O <sub>3</sub>	16.87	15.5	16.90	16.4
V <sub>2</sub> O <sub>5</sub>	32.32	31.3	44.00	43.0

Chemical analyses of the zeolite performed in 36 points (6 points in each of 6 crystals) by means of the EDAX microprobe were averaged to obtain the following formula of the zeolite in the anhydrous form (water cannot be determined by this technique):  $2 \text{Na}_2\text{O} \cdot 2 \text{Al}_2\text{O}_3 \cdot 6 \text{SiO}_2 \cdot \text{V}_2\text{O}_5$ . The data are given in Table III.

Tentative quantitative chemical analysis of the residual solution after the 8 days' decomposition of the Va-5 glass in 2M-NaOH was also carried out; the contents obtained were 10.1%  $\text{SiO}_2$ , 0.3%  $\text{Al}_2\text{O}_3$  and 32.3%  $\text{V}_2\text{O}_5$ . Comparison of these data with the corresponding contents of the Va-5 glass (Table I) indicates that the glass has decomposed virtually completely to the zeolite Nu-15; this is consistent with the microscopic observations. Since the concentration of  $\text{Al}_2\text{O}_3$  is higher in the zeolite

TABLE II

Interplanar distances  $d$  in the zeolites Nu-15 and Nu-10 and the corresponding X-ray diffraction intensities  $I$

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

TABLE III

Chemical composition of zeolite Nu-15

Element	Content, % (m/m)	
	range	average
Na	14.7—16.0	15
Al	18.1—20.3	19
Si	44.3—48.3	46
V	18.5—21.5	20

than in the starting glass, the concentrations of  $\text{SiO}_2$  and  $\text{V}_2\text{O}_5$  in the solution are somewhat higher (fraction corresponding to the dissolved glass from which only Al was used in the lattice of the new phase).

### DISCUSSION

A zeolite containing vanadium in an amount of approximately 20% was prepared by hydrothermal decomposition of vanadium glasses containing 15–17%  $\text{Na}_2\text{O}$ , 15–17%  $\text{Al}_2\text{O}_3$ , 25–40%  $\text{SiO}_2$  and 30–45%  $\text{V}_2\text{O}_5$  at 120–160°C in highly basic NaOH solution ( $1\text{--}4\text{ mol l}^{-1}$ ) for 4–8 days. This zeolite was labelled Nu-15. The position occupied by the vanadium atoms in the zeolite structure could not be determined. The fact that the X-ray diffraction patterns revealed the presence of a single crystalline phase, viz. a zeolite whose interplanar distances  $d$  approach closely those in the zeolite Nu-10, suggests that vanadium, if not incorporated in the zeolite lattice, may be present in the final product in the form of the amorphous oxide. However, multiple washing with hydrochloric acid and sodium perchlorate solution was applied just to prevent this. A single phase was also found by microscopic observation. Thus, it is likely that the vanadium determined analytically in the final product of alteration of the vanadium glass under the above conditions (or a part of it at least) is included in the zeolite, although it is not clear whether it occurs in the structure lattice (and if so, in which positions) or whether it is present in the structure cavities. Quantitative chemical analysis of the zeolite corresponds to the overall formula  $2\text{Na}_2\text{O}\cdot 2\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2\cdot \text{V}_2\text{O}_5$  (see ref.<sup>20</sup>).

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Translated by P. Adámek.