A Convenient Method to Prepare Alkali- and Chloride-free Ammonium Metavanadate (NH_4VO_3)

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A convenient method for the preparation of alkali- and chloride-free ammonium metavanadate has been developed. This new process is utilizing a hydrothermal reaction of vanadium pentoxide with ammonium hydroxide or ammonium carbonate for 2 h at 120 °C in a teflon-lined stainless steel autoclave. The yields are 78 and 82%, respectively.

Because of its role as a common precursor ammonium metavanadate (NH_4VO_3) receives significant attention in the field of inorganic synthetic chemistry. Since the materials produced have structural versatility and various physico-chemical properties they have been applied in catalysis, in electrochemical devices and several other chemical and electronic industries.[1] Quality requirements of the production of high-tech materials, however, have arised the need for new and simple methods providing high purity alkali- and halide-free ammonium metavanadate.

Generally, the preparation of the ammonium metavanadate is based on the extraction of sodium vanadate from vanadium-containing ores or wastes, which is then followed by a precipitation step using ammonium-chloride or other ammonium salts.[2] Crystallization of NH_4VO_3 from the mother liquor of the Solvay process,[3] or the reaction of $VOCl_3$ with NH_4OH solution[4] does not meet the requirements raised by the production of the high purity NH_4VO_3. The aim of the work presented here was to develop a method which can provide an alkali- and chloride-free product.

Reaction of vanadium pentoxide with bases results in the formation of the appropriate salts of vanadic acid, e.g., $NaVO_3$ can be obtained with sodium hydroxide. Ammonium hydroxide, however, does not form NH_4VO_3 at room temperature. This can be attributed to the low basicity. In order to accelerate the dissolution rate of the V_2O_5 the temperature should be increased in a closed system e.g., under hydrothermal conditions to avoid loss of NH_3 from the system.

With increasing temperature and ammonia activity, however, several side reactions have to be reckoned with. These are: (i) redox reactions between the ammonia and the V_2O_5, or between the ammonium ion and the vanadate ion,[5] (ii) polyvanadate ion formation,[6] and (iii) the thermal decomposition of the ammonium metavanadate.[7] At atmospheric pressure the thermal decomposition of the NH_4VO_3 starts at 50 °C,[8,9] and, depending on the pressure–concentration–temperature relationships, various polyvanadates can also be formed.[9,10] Hydrothermal treatment[10] of the NH_4VO_3 at 170 °C leads to the formation of $(NH_4)_{0.5}V_2O_5$.

In order to avoid the polyvanadate formation and the redox reactions between each reducing N–H and oxidizing V–O bond-containing species, the reaction has been performed under autogeneous pressure at 120 °C for 2 h, at more than ten-fold ammonium hydroxide excess. 2.5 g of vanadium pentoxide (Sigma-Aldrich Kft, Hungary) was filled into teflon-lined stainless steel autoclave (volume = 25 mL). Then, 16 mL of 25% aq ammonia solution was added to the V_2O_5. The autoclave was closed and heated in an oil bath. The solid was filtered off, then dried in air without washing.

$$V_2O_5 + 2NH_4OH = 2NH_4VO_3 + H_2O. \qquad (1)$$

Solid NH_4VO_3 formed (1) with a yield of 2.5 g (77.9%). A second crop was harvested by slow evaporation of the mother liquor at room temperature (0.2 g, 6.2%) without the formation of any non-volatile alkali- or halogenide-containing crystallized by-product. XRD of the product can be seen in Figure 1. The X-ray powder diffraction measurements were carried out by a Philips model PW 1050 Bragg–Brentano parafocusing goniometer equipped with a secondary beam graphite monochromator and a proportional counter. Diffraction patterns were recorded in the step mode by using the Cu Kα radiation generated at 40 kV and at a 35 mA tube power. Patterns were evaluated by using the full profile fitting technique. The XRD shows the absence of any other solid crystalline phase. The IR spectrum of the product (4000–400 cm^{-1} diffuse reflectance mode, 5% sample in KBr, Nicolet 170SX FT-IR) is perfectly fitted to the Aldrich FT-IR database spectrum of the NH_4VO_3, and contains both of the N–H (3200 and 1417 cm^{-1}) and polymeric V–O–V (942 cm^{-1}) bonds stretchings and deformations.[11]

In principle, V_2O_5 can not liberate a stronger acid from its salt, however, in the case of ammonium carbonate the evolution of gaseous carbon dioxide shifts the acid–base equilibrium with the formation of ammonium vanadate. Under similar conditions as in the case of ammonia and vanadium pentoxide, the 16 mL 25% aq ammonia solution was substituted with 13 mL of water

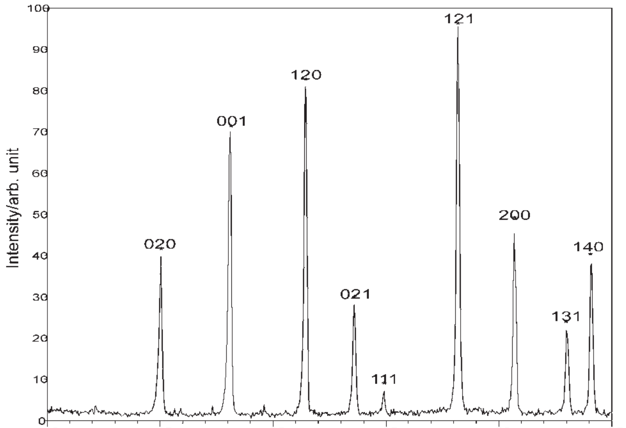

Figure 1. XRD pattern of the synthesized NH_4VO_3.

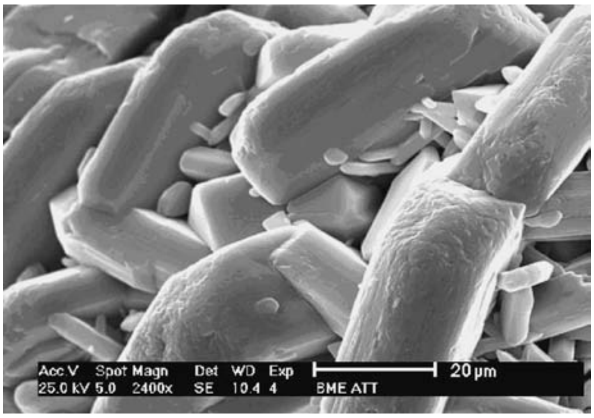

Figure 2. The SEM picture of the synthesized NH_4VO_3.

and 3 g of ammonium carbonate. The yield was 2.8 g (87.2%) NH_4VO_3 (2). Contaminant or the starting ammonium carbonate could not be observed in the product. The second crop provided contaminated NH_4VO_3 with a yield of 0.1 g (ca. 3%).

$$V_2O_5 + (NH_4)_2CO_3 = 2NH_4VO_3 + CO_2 + H_2O. \quad (2)$$

The absence of the latter material may be attributed to the thermal-hydrolitic decomposition of the ammonium carbonate during the drying process at a temperature between 40 and 50 °C. In dry state, the ammonium carbonate decomposition starts at room temperature but finishes only at 58 °C. The presence of water, however, leads to the formation of ammonium hydroxide and carbonic acid which can evaporate/decompose even below 50 °C. The carbonate bands of IR spectra are missing in the spectra of the product, and the spectral features are the same as in the case of the product obtained in the experiment performed with NH_4OH.[11]

A second crop of ammonium metavanadate could also be harvested from the mother liquor (ca. 3%). In this case, however, some distortion of the crystal lattice and changes in d-values were observed (indicating the presence of contaminants). This phenomenon may be the consequence of (i) lower valence polyacids formations (at pH 7–9) and (ii) the decomposition of single crystalline NH_4VO_3 (formed in the slow evaporation of the mother liquor) into V_2O_5 which does not change the crystal lattice (at low temperatures) only distorts it.[10]

The yield of the ammonium carbonate reaction is higher than that of the reaction performed with the ammonium hydroxide. This can be attributed to the decreased solubility of the NH_4VO_3 (it is only 0.52 and 1.6 g/100 mL water at 15 and 50 °C, respectively[12]) due to the ammonium salt[13] added {e.g. excess $(NH_4)_2CO_3$}.

The vanadium pentoxide contains a small amount of $Na_{0.33}VO_3$ which results the presence of 0.13% Na in the starting V_2O_5. The chloride content of the starting V_2O_5 <200 ppm. The sodium content of the NH_4VO_3 obtained from the ammonium hydroxide and the ammonium carbonate reactions are 16.8 and 17.5 ppm, respectively, and no chloride ion was detected in the samples. The sodium content was determined by standard ICP-AES method (Thermo Jarrel Ash Atomscan ICP spectrometer), and the chloride content was measured with standard potentiometric microanalytical method.

The morphology (Figure 2, the SEM pictures were made by Philips XL30 scanning electron microscope) and the spectral characteristics (IR and XRD) of the products obtained from the reactions of NH_4OH and $(NH_4)_2CO_3$ are the same since $(NH_4)_2CO_3$ probably acts a source of NH_4OH. The reaction mechanism might be similar as in the case of the reaction of V_2O_5 and NaF, though only OH^- ion instead of fluoride ion attacks and the ammonium ion neutralizes the formed vanadate anion with formation of crystalline ammonium metavanadate.[14] In this way, hydrothermal reaction of NH_4OH or $(NH_4)_2CO_3$ with V_2O_5 at 120 °C gives highly pure NH_4VO_3 in 78 and 82% yield, resp.

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