

# Vanadium pentoxide application for the synthesis of NaVO<sub>3</sub> in the presence of oxygen

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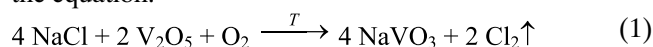
Investigation was carried out on the optimal conditions of the synthesis of NaVO<sub>3</sub> and Cl<sub>2</sub> from NaCl and V<sub>2</sub>O<sub>5</sub> in the presence of the atmospheric oxygen. The influence of the excess of NaCl relative to V<sub>2</sub>O<sub>5</sub> was investigated. Also the effect of the quartz sand introduced into the reaction mixture on the yield of the NaVO<sub>3</sub> synthesis was determined. The obtained product of synthesis was isolated from the post-reaction mixture.

**Keywords:** environment, synthesis, parameter identification, unit operations, sodium metavanadate.

## INTRODUCTION

Trypuć and co-workers investigated the method of sodium carbonate production with the use of NaVO<sub>3</sub>, obtained in a reaction of V<sub>2</sub>O<sub>5</sub> with NaCl, in the presence of steam or oxygen, and a simultaneous production of HCl or Cl<sub>2</sub>. The details of the vanadate method of Na<sub>2</sub>CO<sub>3</sub> synthesis were published in our previous papers<sup>1,2</sup>.

The presented paper is a continuation of Trypuć and co-workers<sup>3,4</sup> research on the determination of optimal parameters for the synthesis of sodium metavanadate(V) from the solid NaCl and V<sub>2</sub>O<sub>5</sub> with the use of oxygen, according to the equation:



It was found that the maximum yield of NaVO<sub>3</sub> could be achieved at 873 K after 5 hours, with the airflow 169 cm<sup>3</sup>·min<sup>-1</sup> through the reactor. For these parameters the yield of the NaVO<sub>3</sub> synthesis is 62.80%.

## EXPERIMENTAL PART

### Chemicals

Analytically pure V<sub>2</sub>O<sub>5</sub> (the purity of 98%), Fluka and NaCl (the purity of 99.5%), POCh Gliwice, Poland, were used without further purification.

### Experimental procedure

The schematic diagram of the reactor, in which the synthesis of NaVO<sub>3</sub> was performed, all the experimental procedure details and the analytical methods were published in our previous papers<sup>3,4</sup>.

The research was conducted in three steps:

1. Determination of the maximum yield of the synthesis with the excess of NaCl used, relative to V<sub>2</sub>O<sub>5</sub>.
2. Determination of the effect of the quartz sand added into the reaction mixture on the yield of the NaVO<sub>3</sub> synthesis.
3. Isolation of NaVO<sub>3</sub> from the post-reaction mixture.

The synthesis of sodium metavanadate(V) was conducted for 5 hours at 873 K, to determine the dependence of the yield of the NaVO<sub>3</sub> synthesis from V<sub>2</sub>O<sub>5</sub> and NaCl in the presence of the air oxygen, on the amount of sodium chloride introduced into the reaction mixture. The airflow through the reactor of 169 cm<sup>3</sup>·min<sup>-1</sup> was constant during the experiments. The synthesis was performed with the use of 10, 20,

30, 40, 50, 100, 150, 200 and 250% excess of NaCl in the reaction mixture, relative to V<sub>2</sub>O<sub>5</sub>.

The second stage of the research was conducted with the airflow fixed at 169 cm<sup>3</sup>·min<sup>-1</sup>, with a reaction time of 5 hours, at 873 K. The constant excess of 100% NaCl, relative to the amount of V<sub>2</sub>O<sub>5</sub>, was used. The inert carrier was added to the reaction mixture in 20, 40, 60, 80, 100, 120, 140 and 160% amount, relative to the total mass of the reaction mixture. The quartz sand, with two-grain size: 0.25 – 0.355 mm and 0.100 – 0.110 mm, was used.

During the NaVO<sub>3</sub> synthesis, all the assumed parameters were measured three times, and the final value was an average of those three obtained data.

The results obtained in that procedure constituted the basis for calculating the yield of the sodium metavanadate(V) synthesis from vanadium(V) oxide and sodium chloride with the use of the atmospheric oxygen.

The samples of the post-reaction mixture were analyzed by the X-ray crystallographic method. Identification of the solid phases was performed for the selected points in the investigated range of temperatures. For the qualitative analysis, all the diffraction patterns were inspected for the series of inter-planar spacing *d* and the relative intensities *I*, and compared with the numerical data contained in „The powder diffraction file”<sup>5</sup>.

The next step of the research was an isolation of pure sodium metavanadate(V) from the post-reaction mixture. The product was separated from the remaining substrates – NaCl and V<sub>2</sub>O<sub>5</sub>.

In order to achieve that, the post-reaction mixture was milled in the FRITSCH mill, and subjected to continuous extraction in the Soxlet apparatus for 72 hours with the use of the distilled water. The obtained extract was concentrated on the water bath. Due to the smallest solubility, vanadium(V) oxide crystallized as the first component of the concentrated extract, and was isolated on the filter paper. Further evaporation led to the precipitation of sodium metavanadate(V), whose solubility is much larger than that of vanadium(V) oxide. The remaining solution contained only sodium chloride, the compound of the largest solubility among the components of the post-reaction mixture<sup>6,7</sup>. Sodium metavanadate(V) isolated in the described procedure was analyzed with the X-ray crystallographic method.

## RESULTS AND DISCUSSION

The results of the research on the effect of an excess of NaCl on the yield of NaVO<sub>3</sub> synthesis from V<sub>2</sub>O<sub>5</sub> and NaCl in the presence of atmospheric oxygen are shown in Table 1.

**Table 1.** The effect of NaCl amount on the yield of the NaVO<sub>3</sub> synthesis (873 K, synthesis time 5 hours, airflow through the reactor 169 cm<sup>3</sup>·min<sup>-1</sup>)

NaCl Excess (%)	Yield (%)
10	65.34
20	69.69
30	73.60
40	74.73
50	76.47
100	81.03
150	80.35
200	79.66
250	76.80

The presented results indicate that the conversion ratio of vanadium(V) oxide into sodium metavanadate(V) is significantly limited by the amount of NaCl present in the reaction mixture.

The yield of NaVO<sub>3</sub> synthesis increases with the increasing amount of the added NaCl up to 100% of its excess, relative to V<sub>2</sub>O<sub>5</sub>. The use of such amount of sodium chloride resulted in the increase of the process yield by 18.23% at 873 K, compared to the synthesis yield with the stoichiometric amounts of the solid reagents.

Further increasing of the sodium chloride excess decreases the V<sub>2</sub>O<sub>5</sub> conversion ratio to NaVO<sub>3</sub>.

The results of the investigation on the effect of the inert carrier excess and the grain diameter on the yield of the NaVO<sub>3</sub> synthesis from V<sub>2</sub>O<sub>5</sub> and NaCl in the presence of the atmospheric oxygen are presented in Table 2.

**Table 2.** The amount and grain diameter effect of the inert carrier on the yield of the NaVO<sub>3</sub> synthesis

Amount (%)	Carrier grain size (mm)	Yield (%)
20	0.25 – 0.355	87.03
	1.00 – 1.10	83.75
40	0.25 – 0.355	89.47
	1.00 – 1.10	85.38
60	0.25 – 0.355	91.65
	1.00 – 1.10	87.60
80	0.25 – 0.355	87.30
	1.00 – 1.10	84.95
100	0.25 – 0.355	84.44
	1.00 – 1.10	82.80
120	0.25 – 0.355	82.31
	1.00 – 1.10	81.76
140	0.25 – 0.355	82.46
	1.00 – 1.10	81.36
160	0.25 – 0.355	81.77
	1.00 – 1.10	80.56

The decrease of the inert carrier grain size results in the increase in the process yield.

The previous research showed that the maximum yield of NaVO<sub>3</sub> synthesis achieved without the use of the inert carrier in the reaction mixture was 81.03% at 873 K.

At 873 K, the addition of the carrier with the grain diameter of 0.25 – 0.355 mm and 1.00 – 1.10 mm, resulted in the yield increase.

The usage of the quartz sand of such grain size in the amount of 60% relative to the reaction mixture increased the yield by 10.62% and 6.57%, respectively.

Further increase of the inert carrier amount results in the decrease in the process yield. This results from the significant volume increase of the reaction mixture, which increases the difficulty of the oxygen penetration into the whole mixture volume.

The first and second steps of the research showed that in order to achieve the maximum yield of the NaVO<sub>3</sub> synthesis from vanadium(V) oxide and sodium chloride in the presence of atmospheric oxygen, the process should be conducted at 873 K, with 100% excess of NaCl relative to V<sub>2</sub>O<sub>5</sub>. Further increase of the yield at that temperature might be achieved by adding the quartz sand of 0.25 – 0.355 mm size into the reaction mixture, in the amount of 60% relative to the total mass of the reaction mixture. For such parameters of the NaVO<sub>3</sub> synthesis, the maximum yield achieved was 91.65%.

The qualitative X-ray diffraction analysis of the post-reaction mixtures revealed the presence of the unreacted V<sub>2</sub>O<sub>5</sub> and NaCl, as well as the synthesized NaVO<sub>3</sub>.

Sodium metavanadate(V) produced in the synthesis according to equation (1) was isolated from the post-reaction mixture in the procedure described in the Experimental section of this paper.

The obtained product was subjected to the X-ray diffraction analysis.

Table 3 presents the diffraction analysis data of sodium metavanadate(V) separated from other components of the post-reaction mixture.

**Table 3.** The inter-planar spacing (d) and the relative intensities (I) of NaVO<sub>3</sub> (CuKα, λ = 0.15418 nm)

Experimental data		Literature data	
d/(nm)	I	d/(nm)	I
0.706	6	0.709	11
0.502	100	0.501	100
0.4265	6	0.4283	6
0.3537	17	0.3542	24
0.3015	13	0.3019	13
0.2952	31	0.2954	35
0.2684	11	0.2683	12
0.2637	4	0.2635	2
0.2539	7	0.2541	7
0.2358	1	0.2360	2
0.2332	6	0.2333	4
0.2294	5	0.2295	5
0.1965	6	0.1965	5
0.1892	5	0.1892	5
0.1824	10	0.1824	6
0.1771	4	0.1771	3
0.1733	2	0.1732	1
0.1715	7	0.1716	5
0.15938	6	0.15944	7
0.14746	3	0.14745	3

The results of the qualitative X-ray diffraction analysis of the investigated compounds prove that the proposed procedure of NaVO<sub>3</sub> separation from the post-reaction mixture allows to obtain the final products with a very high purity level, although do not allow the quantitative separation.

## CONCLUSIONS

1. The products of the reaction, identified in the chemical and instrumental analysis, indicate that the process is consistent with the general equation (1).
2. The yield of the process is strictly limited by the amount of NaCl used in the reaction. The yield of the described NaVO<sub>3</sub> synthesis at 873 K increases with the increasing amount of NaCl up to its 100 % excess, relative to vanadium(V) oxide.
3. The significant increase of the process yield is achieved with the use of the inert carrier in the reaction mixture.
4. The maximum yield of the NaVO<sub>3</sub> synthesis from vanadium(V) oxide and sodium chloride in the presence of atmospheric oxygen was achieved at 873 K with 100% excess of NaCl relative to V<sub>2</sub>O<sub>5</sub>. Further increase of the synthesis yield at that temperature was achieved by an addition of the quartz sand with the grain diameter 0.25 – 0.355 mm in the amount equal 60% of the total mass of the reaction mixture. Under these conditions the maximum yield of the NaVO<sub>3</sub> synthesis is 91.65%.
5. The proposed procedure of NaVO<sub>3</sub> separation from the post-reaction mixture allows obtaining the final product of very high purity.

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