Vanadium pentoxide application for the synthesis of NaVO₃ in the presence of oxygen

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Investigation was carried out on the optimal conditions of the synthesis of NaVO₃ and Cl₂ from NaCl and V₂O₅ in the presence of the atmospheric oxygen. The influence of the excess of NaCl relative to V₂O₅ was investigated. Also the effect of the quartz sand introduced into the reaction mixture on the yield of the NaVO₃ 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 NaVO₃, obtained in a reaction of V₂O₅ with NaCl, in the presence of steam or oxygen, and a simultaneous production of HCl or Cl₂. The details of the vanadate method of Na₂CO₃ synthesis were published in our previous papers³,⁴. The presented paper is a continuation of Trypuć and co-workers³,⁴ research on the determination of optimal parameters for the synthesis of sodium metavanadate(V) from the solid NaCl and V₂O₅ with the use of oxygen, according to the equation:

\[ 4 \text{NaCl} + 2 \text{V}_2\text{O}_5 + \text{O}_2 \rightarrow 4 \text{NaVO}_3 + 2 \text{Cl}_2 \]  \hspace{1cm} (1)

It was found that the maximum yield of NaVO₃ could be achieved at 873 K after 5 hours, with the airflow 169 cm³·min⁻¹ through the reactor. For these parameters the yield of the NaVO₃ synthesis is 62.80%.

EXPERIMENTAL PART

Chemicals

Analytically pure V₂O₅ (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 NaVO₃ was performed, all the experimental procedure details and the analytical methods were published in our previous papers³,⁴. The research was conducted in three steps:

1. Determination of the maximum yield of the synthesis with the excess of NaCl used, relative to V₂O₅.
2. Determination of the effect of the quartz sand added into the reaction mixture on the yield of the NaVO₃ synthesis.
3. Isolation of NaVO₃ 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 NaVO₃ synthesis from V₂O₅ 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 cm³·min⁻¹ 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 V₂O₅.

The second stage of the research was conducted with the airflow fixed at 169 cm³·min⁻¹, with a reaction time of 5 hours, at 873 K. The constant excess of 100% NaCl, relative to the amount of V₂O₅ 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 NaVO₃ 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”⁶. 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 V₂O₅.

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 mixture⁶,⁷. 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 NaVO₃ synthesis from V₂O₅ 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 NaVO₃ synthesis (873 K, synthesis time 5 hours, airflow through the reactor 169 cm³·min⁻¹)

| 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             | 78.80     |

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 NaVO₃ synthesis increases with the increasing amount of the added NaCl up to 100% of its excess, relative to V₂O₅. 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 V₂O₅ conversion ratio to NaVO₃.

The results of the investigation on the effect of the inert carrier excess and the grain diameter on the yield of the NaVO₃ synthesis from V₂O₅ 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 NaVO₃ synthesis

| Amount (%) | Carrier grain size (mm) | Yield (%) |
|------------|-------------------------|-----------|
| 20         | 0.25 – 0.355            | 87.03     |
| 40         | 0.25 – 0.355            | 89.47     |
| 60         | 0.25 – 0.355            | 91.65     |
| 80         | 0.25 – 0.355            | 87.30     |
| 100        | 0.25 – 0.355            | 84.95     |
| 120        | 0.25 – 0.355            | 82.80     |
| 140        | 0.25 – 0.355            | 81.77     |
| 160        | 0.25 – 0.355            | 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 NaVO₃ 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 NaVO₃ 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 V₂O₅. 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 NaVO₃ 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 V₂O₅ and NaCl, as well as the synthesized NaVO₃.

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 NaVO₃ (CuKα, λ = 0.15418 nm)

| Experimental data | Literature 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 |
| 0.2232 | 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 NaVO₃ 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 NaVO₃ 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 NaVO₃ 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 V₂O₅. 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 NaVO₃ synthesis is 91.65%.

5. The proposed procedure of NaVO₃ separation from the post-reaction mixture allows obtaining the final product of very high purity.

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