

OXIDATION OF 4-METHYLPYRIDINE ON V-Cr-O CATALYST

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Abstract. Isonicotinic acid derivatives are used in the development of new antibacterial agents, active ingredients in pesticides and herbicides. In addition, isonicotinic acid is a precursor for the synthesis of isoniazid, one of the most effective anti-TB drugs. Considering the importance of isoniazid in the treatment of tuberculosis, improving methods of synthesizing isonicotinic acid has a direct impact on the availability and cost of this life-saving drug. *The goal* of this work was to investigate the efficiency of V-Cr-O catalyst in the oxidation of 4-methylpyridine to produce isonicotinic acid, to study its composition and properties. *Research methods.* Methods of chemical analysis, scanning electron microscope (SEM), Raman spectroscopy were applied. *Results and Discussion.* In this work, the processes of isonicotinic acid synthesis by oxidation of 4-methylpyridine on the V-Cr-O catalyst were studied. Analysis of the obtained results showed that with an increase in the water feed, there is a general tendency towards a decrease in the conversion of 4-methylpyridine at all temperatures. For example, at a temperature 300°C, the degree of conversion drops from 91.72% at 1.79 g/h to 84.20% at 6.6 g/h. The yield of isonicotinic acid increases as the amount of water rises, reaching its peak at 47.46% with a temperature of 360°C and a water supply of 6.6 g/h. In contrast, the minimum yield is only 15.27% at 280°C with a water supply of 1.79 g/h. This highlights the positive correlation between water supply and yield, especially at higher temperatures.

Key words: isonicotinic acid, 4-methylpyridine, oxidation; vanadium catalyst, Pechini method.

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1. Introduction

Over the years, water quality has deteriorated mainly due to anthropogenic. The oxidation of 4-methylpyridine (4-MP) is essential for producing isonicotinic acid, a precursor for various pharmaceuticals, including anti-tuberculosis drugs [1]. Vanadium oxide-based catalysts, especially those modified with chromium oxides, have shown promising activity and selectivity in this reaction [2-4]. The V-Cr-O catalytic system efficiently oxidizes 4-MP, leveraging the combined effects of vanadium and chromium oxides to enhance overall catalytic performance [5-7].

Research has shown that adding chromium to vanadium oxide catalysts improves the dispersion of active sites and increases the catalyst's thermal stability [8]. This modification results in a more robust catalytic system that maintains high activity over extended periods [9]. The unique properties of V-Cr-O catalysts, particularly their ability to selectively oxidize 4-MP to isonicotinic acid, make them highly suitable for industrial applications.

In this study, we will investigate the catalytic performance of V-Cr-O catalysts in the oxidation of 4-methylpyridine. We will explore how different reaction parameters, such as temperature and reactant concentration, affect the yield and selectivity of the desired product. To achieve this, we will conduct detailed catalytic tests and use techniques like Raman spectroscopy, scanning electron microscopy (SEM), and thermal analysis (TG-DSC). This approach will help us gain a deeper understanding of the relationship between structure and catalytic activity.

2. Experimental part

The catalytic systems were synthesized using the Pechini method [10-13]. The V:Cr:CA ratio was maintained at 1:1:10 throughout the preparation process. All chemicals were of analytical grade and used as received without further purification. 10 mole of citric acid (CA) was dissolved in 100 ml of distilled water in a 500 ml beaker, with the mixture being stirred at 70°C until the citric acid was completely dissolved. Subsequently, 1 mole each of $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were added to the solution. After ensuring complete dissolution, 10 mole of ethylene glycol (EG) with CA:EG 1:1 ratio was introduced. The mixture was then heated to 90°C to evaporate excess moisture. The resulting resin was then dried at 120°C for a duration of 12 hours. The dried product was then subjected to heating at 400°C for 4 hours, followed by calcination at 800°C for 4 hours to obtain the final catalyst.

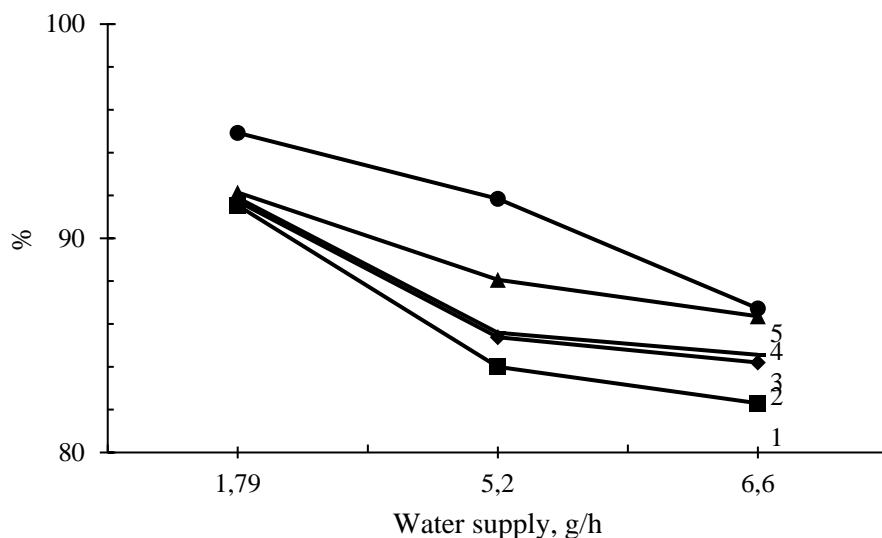
Products of the reaction were collected in airlift-type scrubbers irrigated with water. Chromatographic analysis of oxidation products of 4-methylpyridine was performed using the "Cvet-106" chromatograph. Isonicotinic acid was detected using a "pH-150MI" pH meter and titrated with KOH. The samples' structure was analyzed using a Raman spectrometer called Solver Spectrum (NT-MDT company). Images of the catalyst surface morphology were obtained using a

Quanta 3D 2001 scanning electron microscope. The thermal stability of the catalyst was analyzed using a Thermo gravimetric analyzer (TGA) SKZ1053.

3. Results and Discussion

The test results of individual V-Cr-O catalyst in the oxidation of 4-methylpyridine are shown in Figures 1 and 2.

The Fig. 1 shows how the amount of water affects the conversion rate of 4-methylpyridine at five different temperatures. Across all temperatures, the conversion rate decreases as the water supply increases, suggesting that more water reduces conversion efficiency. Interestingly, while all temperatures exhibit this decline, the higher temperatures tend to maintain slightly better conversion rates than the lower ones.



1 – 280°C, 2 – 300°C, 3 – 320°C, 4 – 340°C, 5 – 360°C.

Fig. 1. Effect of temperature and water supply rate on 4-methylpyridine conversion

For instance, at 340°C (4), the conversion starts at 92.86% with 1.79 g/h and only falls to 86.36% when the water supply increases to 6.6 g/h, showing a moderate decline. In contrast, at 280°C, the conversion rate drops more sharply, from about 91.53% at 1.79 g/h down to 82.30% at 6.6 g/h. This indicates that lower temperatures experience a more significant impact from increased water.

The Fig. 2 illustrates the relationship between the water supply and the yield of isonicotinic acid across five different temperatures. As the water consumption increases, there is a general trend of increasing yields for isonicotinic acid at all temperatures. At temperature 280°C, the yield remains relatively constant at about 15-20% regardless of the amount of water. At Temperatures 300°C and 320°C, the yield of isonicotinic acid increases slightly from 20.73% to 22.91% and

24.00% to 24.55% respectively, as the water supply increases from 1.79 g/h to 5.2 g/h. Then, the yield increases sharply to 36.55% and 39.81% respectively, as the water feed rate increases to 6.6 g/h. At 340°C, the yield of isonicotinic acid starts at 27.27% with a water feed rate of 1.79 g/h and goes up to 44.18% at 6.6 g/h. At 360°C, it begins at 28.91% and increases to over 47.46% with the same water feed rate.

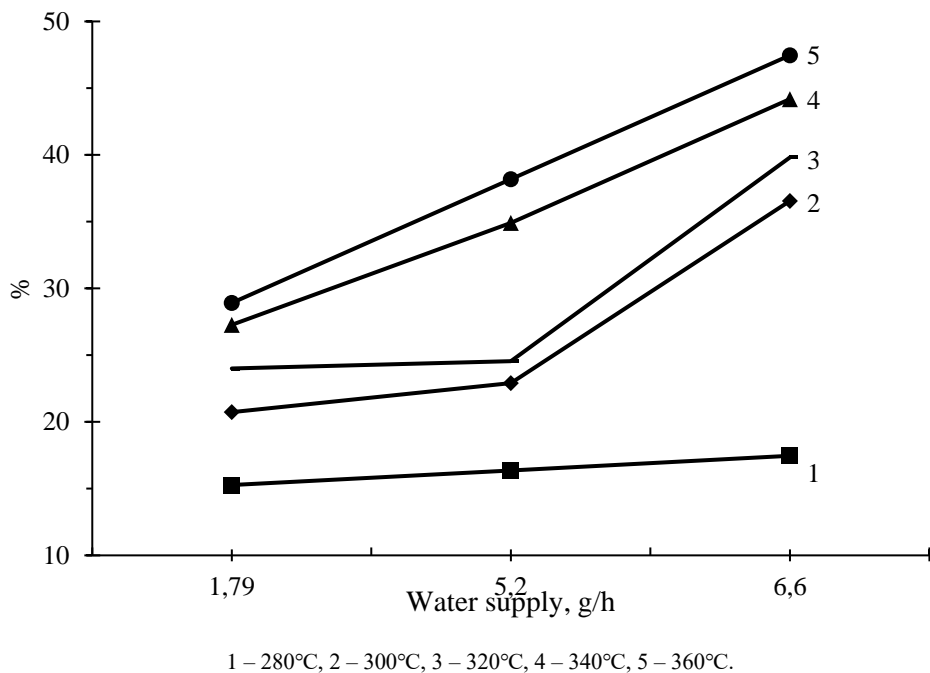


Fig. 2. Effect of temperature and water supply rate on isonicotinic acid yield

Raman spectroscopy analysis. A typical Raman spectrum of V-Cr-O catalyst confirms vanadium oxide presence in the catalyst framework with a strong peak observed near 1000 cm^{-1} [14,15], which correspond to the vibrational stretching modes of V=O bond. Other relatively weak peaks found between 800 cm^{-1} and 600 cm^{-1} which are attributed to the symmetric and asymmetric stretching vibrations of the Cr-O bonds [16], that affirm the presence of chromium oxides. These results were consistent with the observations of Weckhuysen and Wachs [17], who also reported such bands in the Raman spectra of supported chromium oxide, thus confirming that both vanadium and chromium oxides were successfully synthesized and integrated in V-Cr-O catalyst as expected.

Such considerations and the absence of more peaks indicate the high quality of the catalyst and almost absolute lack of by another phases or impurities, which stem from controlled synthetic procedures and appropriate distribution of the metal oxides within the catalytic matrix. Overall, the data obtained from the Raman spectra provides useful information concerning the molecular

configuration and composition of the V-Cr-O catalyst including the content of metal oxides of expected types and the vibrational modes associated with them.

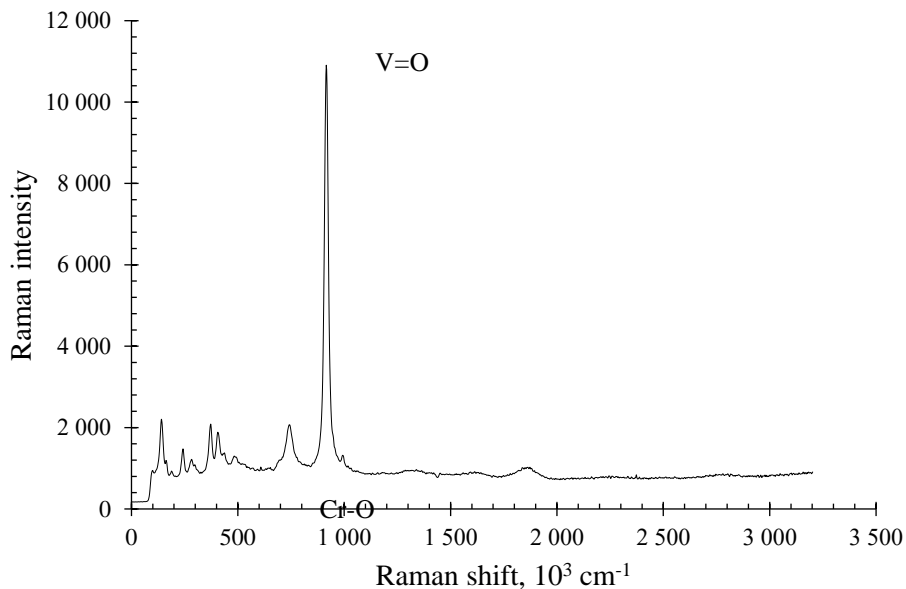


Fig. 3. Raman spectra of synthesized V-Cr-O catalyst

SEM analysis. To examine the morphology of the obtained V-Cr-O catalyst, scanning electron microscopy analysis was used. In Fig. 4, we can see sample particles with non-uniform sizes. The SEM images reveal particles with varying sizes and irregular shapes, showcasing a complex surface structure. Some particles appear flaky or layered, while others are more compact and dense. The particles range from approximately 200 nm to 500 nm.

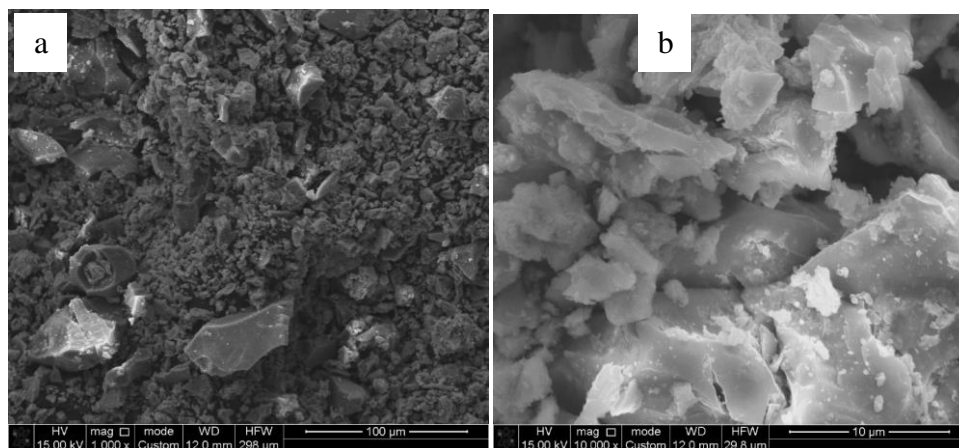


Fig. 4. SEM images of V-Cr-O catalyst: a – 1 000x, b – 10 000x

This variation in particle size and morphology suggests a heterogeneous sample, which could influence the catalyst's surface area and reactivity. The presence of both smooth and rough surfaces may indicate different phases or compositions within the sample. Notably, the absence of distinct shapes like spheres or needles indicates that the V-Cr-O catalyst particles are amorphous and lack a well-defined crystalline structure.

XRD analysis. XRD analysis of the V-Cr-O catalyst was performed, and the results are shown in the Fig. 5. The XRD patterns reveal several distinct peaks, indicating the crystalline nature of the sample. The diffraction peaks of the V-Cr-O catalyst closely match standard vanadium and chromium oxide peaks. Only 2 peaks were observed that correspond to chromium vanadate CrVO_4 (84-1740) and vanadium oxide V_2O_5 (77-2415). In the case of vanadium oxide, the peaks correspond to the orthorhombic phase. Similarly, the peaks for chromium oxide are indexed for rhombohedral phase.

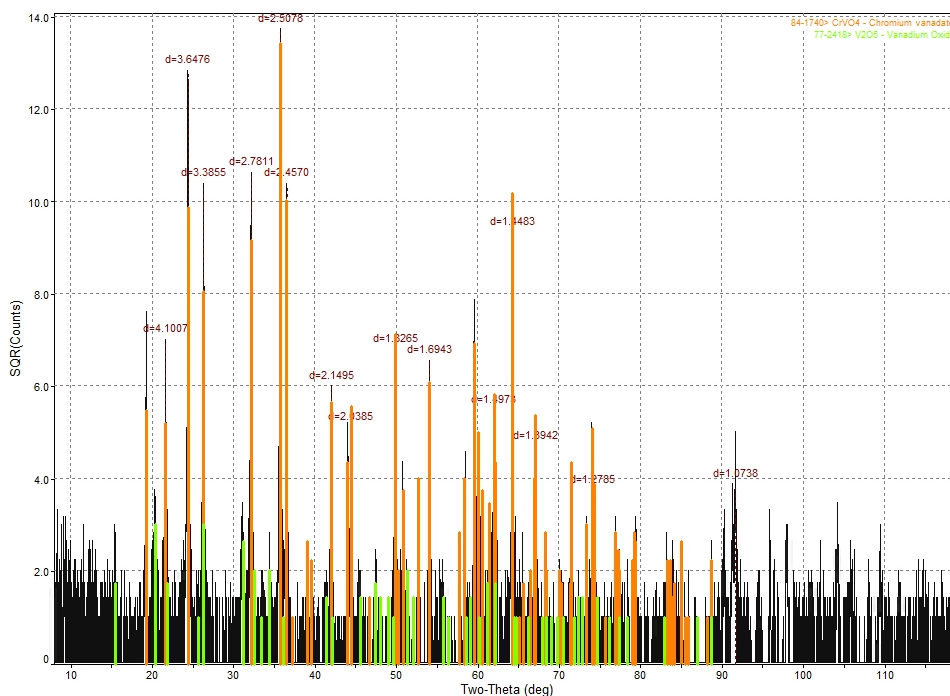


Fig. 5. XRD pattern of V-Cr-O catalyst

From the patterns, it is also noticed that V-Cr-O catalyst consists of been V_2O_5 as the dominant phase along with CrVO_4 phase as well. No extra peaks referred to some impurities were noticed thereby indicating the sample was pure since no other impurities were present. The shape of the peaks demonstrated the high crystallinity of the V-Cr-O catalyst.

TG-DTG analysis. The V-Cr-O catalyst was qualitatively characterized using thermal techniques, as presented in the Fig. 6. The experiments were done employing nitrogen as carrier gas. The TG-DTG curves indicate the thermal stability and thermal decomposition of the V-Cr-O catalyst. From the DTG curve it is seen quite a number of endothermic and exothermic effects:

Initial Mass Loss: From the TGA curves there is initial loss of mass up to approximately 10 minutes and results in mass reduction of about 10%. This initial loss is due to the removal of adsorbed water or other volatile components.

Major Decomposition Step: The mass loss is most pronounced between 10 and 20 minutes after which around 30% of the total mass is lost. This step has a sharp endothermic interfaced about 10 minutes promoting mass loss correlating with decomposition of V-Cr-O structural compounds.

Stabilization: The mass loss reaches an apparent plateau after 23 minutes, revealing that the major decomposition processes have been completed.

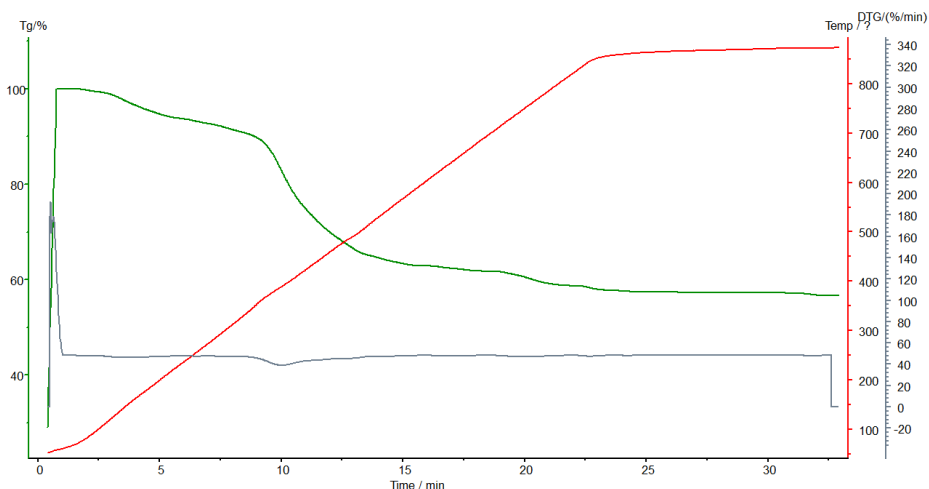


Fig. 5. TG-DTG curves of V-Cr-O catalyst

4. Conclusion.

The analysis shows that increasing water supply reduces the conversion efficiency of 4-methylpyridine at all temperatures. However, higher temperatures lessen this decline, with only a moderate drop at 340°C compared to a sharper decrease at 280°C. Higher water supply generally boosts the yield of isonicotinic acid, particularly at elevated temperatures. At 280°C, the yield stays steady at around 15-20%. However, it rises more noticeably at 300°C, 320°C, 340°C, and 360°C, reaching over 47.46% at 360°C with increased water. Raman spectroscopy confirms that the V-Cr-O catalyst was successfully synthesized, with vanadium and chromium oxides well integrated into the structure. The SEM analysis of the V-Cr-O catalyst shows that the sample is quite mixed, with particles ranging in size from about 200 nm to 500 nm and having different shapes and surface

textures. Interestingly, there aren't any clear shapes like spheres or needles, which suggests that the particles are amorphous and don't have a well-defined crystalline structure. The XRD analysis of the V-Cr-O catalyst shows that the sample is highly crystalline, mainly made up of vanadium oxide (V_2O_5) and chromium vanadate ($CrVO_4$). The absence of any extra peaks suggests the catalyst is very pure, with little to no impurities and unwanted phases. The TG-DTG analysis of the V-Cr-O catalyst shows that it has decent thermal stability. After about 23 minutes, the mass loss levels off, which means the remaining material is stable and won't degrade much further.

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Conflict of Interest: All authors declare that they have no conflict of interest.

4-МЕТИЛПИРИДИНДИ V-Cr-O КАТАЛИЗАТОРЫНДА ТОТЫҚТЫРУ

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Түйіндеме. Изоникотин қышқылының туындылары жаңа бактерияға қарсы агенттер мен пестицидтер мен гербицидтердің белсенді ингредиенттерін жасауда қолданылады. Сонымен қатар, изоникотин қышқылы туберкулезге қарсы ең тиімді препараттардың бірі болып табылатын изониазид синтезінің прекурсоры болып табылады. Туберкулезді емдеуде изониазидтің маңыздылығын ескере отырып, изоникотин қышқылын синтездеу әдістерін жетілдіру осы өмірлік маңызды препараттың қолжетімділігі мен құнына тікелей әсер етеді. Жұмыстың мақсаты изоникотин қышқылын алу үшін 4-метилпиридинді тотығуда V-Cr-O катализаторының тиімділігін анықтау және оның құрамы мен қасиеттерін зерттеу. *Зерттеу әдістері.* Химиялық талдау әдістері, сканерлеуші электронды микроскоп (СЭМ) және Раман спектроскопиясы қолданылды. *Нәтижелер мен талқылаулар.* Бұл жұмыста 4-метилпиридиннің V-Cr-O катализаторында тотығуы арқылы изоникотин қышқылының синтезделу процестері зерттелді. Алынған нәтижелерді талдау сумен қамтамасыз етудің жоғарылауымен барлық температурада 4-метилпиридиннің конверсиясының төмендеуіне жалпы тенденция бар екенін көрсетті. Осылайша, 300°C температурада конверсия дәрежесі 1.79 г/сағ кезінде 91.72%-дан 6.6 г/сағ кезінде 84.20%-ға дейін төмендейді. Изоникотин қышқылының шығымы судың мөлшері артқан сайын артып, 360°C температурада және 6.6 г/сағ су беру кезінде 47.46% шыңға жетеді. Керісінше, ең төменгі өнімділік 280°C температурада тек 15.27% және сумен қамтамасыз ету 1.79 г/сағ. Бұл әсіресе жоғары температурада су беру мен шығым арасындағы оң корреляцияны көрсетеді.

Түйін сөздер: изоникотин қышқылы, 4-метилпиридин, тотығу; ванадий катализаторы, Печини әдісі.

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ОКИСЛЕНИЕ 4-МЕТИЛПИРИДИНА НА КАТАЛИЗАТОРЕ V-Cr-O

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Резюме. Производные изоникотиновой кислоты используются при разработке новых антибактериальных средств, действующих веществ в пестицидах и гербицидах. Кроме того, изоникотиновая кислота является предшественником для синтеза изониазида — одного из самых эффективных противотуберкулезных препаратов. Учитывая важность изониазида в лечении туберкулеза, совершенствование методов синтеза изоникотиновой кислоты напрямую влияет на доступность и стоимость этого жизненно важного препарата. *Целью* данной работы было исследование эффективности катализатора V-Cr-O в окислении 4-метилпиридина с получением изоникотиновой кислоты, изучение его состава и свойств. *Методы исследования.* Применялись методы химического анализа, сканирующий электронный микроскоп (СЭМ), Рамановская спектроскопия. *Результаты и обсуждение.* В данной работе изучены процессы синтеза изоникотиновой кислоты окислением 4-метилпиридина на катализаторе V-Cr-O. Анализ полученных результатов показал, что с увеличением подачи воды наблюдается общая тенденция к снижению конверсии 4-метилпиридина при всех температурах. Так, при температуре 300°C степень конверсии падает с 91.72% при 1.79 г/ч до 84.20% при 6.6 г/ч. Выход изоникотиновой кислоты увеличивается с ростом количества воды, достигая пика в 47.46% при температуре 360°C и подаче воды 6.6 г/ч. Напротив, минимальный выход составляет всего 15.27% при 280°C и подаче воды 1.79 г/ч. Это подчеркивает положительную корреляцию между подачей воды и выходом, особенно при более высоких температурах.

Ключевые слова: изоникотиновая кислота, 4-метилпиридин, окисление; ванадиевый катализатор, метод Печини.

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