About the Routes of Oxidative Conversion of 2-methyl-5-ethylpyridine on Vanadium Oxide Modified Catalyst

D.Kh. Sembaev*, O.K. Yugay and S.G. Klepikova

Institute of Chemical Sciences the Academy of Science, 106 Ualikhanov St., 480100, Almaty, Kazakhstan

Abstract

The vapor phase oxidation of 2-methyl-5-ethylpyridine (MEP) on modified vanadium oxide catalyst has been investigated. Di(5-ethyl)-2-pyridil, 2-methyl-5-acetylpyridine and 3-acetylpyridine have been identified as intermediates of MEP oxidation by NMR $^{13}$C spectroscopic and gas chromatography mass spectrometry methods. It has been shown that the interaction between the pyridine base and acidic proton donating sites on the catalyst surface causes an increase of substituents reactivity in 2-position in all stages of 2-methyl-5-ethylpyridine transformation inducing their oxidative elimination. A distinction in composition of the oxidation products is an outcome of a change of the dialkylpyridine substituents in 2- and 5-position contribution. Using literature and experimental data the basic routes of the 2-methyl-5-ethylpyridine oxidative conversion have been determined. The ammoxidation is a process based on the joint oxidation of the initial organic substance and ammonia by air oxygen in the presence of a catalyst [1]. The basic step of ammoxidation is a vapor phase catalytic oxidation, which determines the main routes of the former. Therefore, the obtained results give a possibility for the first time to explain the reason for the change of selectivities during MEP ammoxidation in the present of water.

Introduction

2-Methyl-5-ethylpyridine (MEP) is synthetic product which is interesting as a starting substance for the production of nicotinic acid and its nitrile. A number of investigations [2-5] have been devoted to the details of the dialkylpyridine conversion in oxidative ammonolysis on the various catalysts. It has been determined that due to increased reactivity of the methyl group the oxidative conversion of MEP proceeds through the sequential formation of 2-cyano-5-ethyl-, 2-cyano-5-vinyl-, 2.5-dicyano- and 3-cyanopyridines. The reaction starts with the transformation of MEP ethyl group and following by the formation of 2-methyl-5-vinyl-, 2-methyl-5-cyano- and 2-cyano-5-vinylpyridines intermediates which have much less share. Apparently, part of 2.5-dicyanopyridine is formed by simultaneous involving of the both alkyl groups in the reaction. Depending on the conditions of the catalytic process the basic reaction products are 2.5-dicyano- and 3-cyanopyridines. Some questions concerning the mechanism of the MEP oxidative conversion have been investigated insufficiently, perhaps because of incomplete analysis of reaction products. An existence of some intermediates of MEP oxidation, for example 2-methyl-5-acetylpyridine, has been assumed only hypothetically.

The influence of the process conditions upon the degree of participation of the substituents in the 2- and 5-positions of MEP molecule in the formation of certain products of oxidation and ammoxidation of dialkylpyridine was insufficiently defined. At present the new active catalysts, which are able to work at the comparatively low temperature, have been developed in the laboratory of petrochemical synthesis of the ICS MES RK. That fact revived the interest in MEP as a raw material for producing of nicotinic acid and its nitrile. Therefore the determination of the routes of the MEP oxidative conversion is a problem which can help the choice of better catalyst and conditions of the oxidative process.

The aim of the present work is to determine the basic routes of the MEP conversion by the detail analysis of the oxidation products at the various catalytic conditions in order to reveal the influence of the process conditions on the selectivity of MEP conversion.
Experimental

MEP dried and distilled at 142°C (695 mm Hg) was used in the present work. The flow set with the reaction tube of stainless steel 20 mm in diameter and 1100 mm in length was used for conducting of the oxidation [6]. The reactor was loaded with 100 mL of a granulated vanadium oxide catalyst with the size of catalyst particles of 3-5 mm modified by the titanium and zirconium oxides [7].

MEP oxidation was carried out with MEP feeding of 29.5 g on 1 L of catalyst/h, temperature – 210-270°C, molar ratio of MEP:O2:H2O = 1:50:0-150 and contact time 0.44-0.67 s.

The reaction products were collected in the scrubber, sprayed with water. The reaction products were analyzed by a gas chromatographic method on chromatograph LHM-80 with a flame-ionization detector in the isothermal regime (temperature – 140°C). Chromatographic columns with the length of 2 m and diameter of 3 mm were filled with a phase 10% Lucopren G-1000 on Chromaton N-AW-HMDS (0.20-0.25 mm). Isochincherononic and nicotinic acids were analyzed by the polarographic method. CO2 was determined by the method of gas adsorptive chromatography. The structure of di(5-ethyl)-2-pyridil was established by the IR- and NMR 13C spectroscopic methods. The NMR spectra were recorded on the Mercury 300 equipment of VARIAN Company in a deuterated chloroform. 2-Methyl-5-acetyl- and 3-acetylpyridines were analyzed by the gas chromatography-mass spectrometry on Hewlett-Packard 5890, Series II in a methylene chloride.

Results and Discussion

The effect of the various parameters of the vapor phase catalytic oxidation on selectivity of the products formation has been investigated to bring out the basic routes of the MEP conversion. In order to establish a sequence of the products formation the experimental results have been presented as the dependences of the products selectivity's on degree of the MEP conversion.

An analysis of the reaction products has shown that 2-methyl-5-vinylpyridine, pyridine-2-aldehyde, isocinchomeronic and nicotinic acids, pyridine, CO2 as well as di(5-ethyl)-2-pyridil, first isolated and identified by us, are the products of the MEP oxidation.

On Fig. 1 the results of the MEP oxidation on the modified vanadium oxide catalyst are presented. At low conversions of the starting compound the selectivity to pyridine-2-aldehyde reaches almost 30%, and that of the di(5-ethyl)-2-pyridil formation exceeds that value. The total selectivity to the above-mentioned products is 60%, which suggests a predominant attack of oxygen to the methyl group in the 2-position. The selectivity to isocinchomeronic acid is 10-12%, but at the high conversion of MEP it decreases to 8%. The results of those experiments reveal proceeding of a selective conversion of the both alkyl groups to carboxy-groups.

It is known that pyridine-2-aldehyde is able to undergo a typical benzoin condensation [8]. The Indian investigators [9] have reported that in the catalytic vapor phase oxidation of 2-methylpyridine on the modified vanadium oxide catalysts 2-pyridoin has been found. Similar reactions can proceed in MEP oxidation on the vanadium oxide catalyst modified by the titanium and zirconium oxides. At a low MEP conversion (conversion – 30%) one of the basic products of oxidation is di(5-ethyl)-2-pyridil (diketone). It can be generated as a result of benzoin condensation of 5-ethylpyridine-2-aldehyde through the intermediary stage of diethylpyridoin formation:

As a MEP conversion becomes higher, the selectivity to diketone decreases. And when the conversion reach 45%, diketone is absent in the reaction products. At the same time the selectivity to CO2 increases sharply. At 90-100% conversion of MEP the selectivity to CO2 reaches 70%. In a wide range of the conditions traces of nicotinic acid is present among the reaction products. The selectivity of its
formation does not exceed 1-2%.

An introduction of steam into the contact zone causes an abrupt change of the oxidative process (Fig. 2). Alongside with the above defined reaction products there appear 2-Methyl-5-acetylpyridine, 3-acetylpyridine, pyridine-3-aldehyde and nicotinic acid, whose selectivity reaches 50%. 2-Methyl-5-acetylpyridine was identified the first time by us as an intermediate in MEP oxidation. The selectivity to 2-methyl-5-vinylpyridine increases slightly. The formation of these products is the evidence of an oxygen attack to the both alkyl groups. The basic manifestations of a steam effect on the catalytic process are the absence of isocinchomeronic acid in the reaction products and the formation of nicotinic acid with high selectivity, which testifies to the fact that reactivity of the substituents in the 2-position of the pyridine cycle significantly increases. A sudden decrease of the selectivity to pyridine-2-aldehyde, being accompanied by rise of the CO₂ formation, also confirms it.

It is known that the acidic proton donating sites are formed by water molecule adsorption on the oxide catalyst surface [10]. The observed changes in the features of the oxidative process are caused by the increasing of the surface acidity. An interaction between pyridine base and catalyst acid sites results in the substantial increase of reactivity of the substituent in the 2-position [11,12]. In consequence of that, as one can see from the comparison of Fig. 1 and Fig. 2, the catalyst composition changes noticeably, which is the evidence for the change of the route of MEP oxidative transformation. The data from the report [13] support it. The authors have shown that the higher reactivity of methyl group in comparison with ethyl one is caused by the interaction of MEP heteroatom and acid site of the catalyst surface.

A comparison of the change of the selectivities at the different MEP conversion degrees give a basis to propose that the process proceeds in the following basic routes (Fig. 3).
When the oxidation is conducted in the absence of water, the increase of MEP conversion is accompanied by the decreasing of selectivity to diketone and the simultaneous increase of isocinchomeronic acid and CO$_2$ formation. Apparently, diketone, undergoing the oxidative transformations, is the main source for isocinchomeronic acid and CO$_2$ obtaining. Pyridine-2-aldehyde also yields some contribution in CO$_2$ formation.

When the MEP oxidation proceeds in the presence of water, due to an increase of a methyl group reactivity, the formed 2-methyl-5-acethylperidine is converted, into 3-acetylpyridine. With the further oxidation of the latter nicotinic acid is formed.

2-Methyl-5-vinylpyridine is also converted to nicotinic acid through the step of pyridine-3-aldehyde formation.

Diketone forms both into nicotinic acid and into pyridine-2-carbonic acid, the latter is easily decarboxylated.

Thus, an interaction of unshared electron pair of a MEP nitrogen atom and catalyst acid site increases a reactivity of any substituent in 2-position, which leads to its elimination.

The ammoxidation is a process based on the joint oxidation of the initial organic substance and ammonia by air oxygen in the presence of a catalyst. The basic step of ammoxidation is a vapor phase catalytic oxidation, which determines the main routes of the former. Therefore, the obtained results give a possibility for the first time to explain the reasons for the change of selectivities during MEP ammoxidation under the influence of the water introduced into the reaction zone. In the absence of water 5-ethyl-2-cyanopyridine and 2,5-dicyanopyridine are the main products of ammoxidation (Fig. 4), just as di(5-ethyl)-2-pyridil and isocinchomeronic acid are those of the oxidation.

In the experiments with the water introduction the mechanism of MEP ammoxidation substantially changes due to the interaction between a pyridine base and an acidic proton donating site of the catalyst surface, which leads to an increase of substituents reactivity in 2-position in all steps of the dialkylpyridine transformation, causing the oxidative elimination of those substituents. In that case the main reaction product is nitrile of nicotinic acid, the yield of which can reach 80% [7].

**Conclusions**

The basic routes of the 2-methyl-5-ethylpyridine
oxidative conversion have been determined. As follows from the obtained data the interaction between the pyridine base and acidic proton donating sites on the catalyst surface causes an increase of substituents reactivity in 2-position in all stages of 2-methyl-5-ethylpyridine transformation inducing their oxidative elimination.

References

1. Suvorov B.V. Ammoxidation of organic compounds. Nauka, Alma-Ata, 1971, p. 148
2. Pavlov E.A., Serazetdinova V.A., Kargarlitsky A.D., Suvorov B.V. Khim. Heter. Soed. 4:665 (1968)
3. Suvorov B.V., Kargarlitsky A.D., Kutjanov R.T., Djumakaev K.H., Neverdovsky G.G. Izvestiya AN KazSSR. Ser. Khim. 6:67 (1976)
4. Djumakaev K.H., Kargarlitsky A.D., Suvorov B.V. Izvestiya AN KazSSR. Ser. Khim. 3:53 (1977)
5. 5.Suvorov B.V., Kargarlitsky A.D., Kan I.I. Kinet. Katal. 18:4:957 (1977)
6. Kargarlitsky A.D., Kudinova V.S., Sembaev D.Kh., Suvorov B.V. Izvestiya AN SSR. Ser. Khim. 2:23 (1966)
7. Sembaev D.Kh., Ivanovskaya F.A., Guseinov E.M., Chuck R.D. Pat. Schweiz 0760709
8. R.C.Elderfield (ed.), Heterocyclic compounds, Forein Literature, Moscow, 1953, v. 1, p. 458
9. Bhattacharya S.K., Shankar V., Kar A.K. Ind. Eng. Chem. Prod. Res. Devel. 5:1:65 (1966)
10. Kiselev V.F. Doklady AN SSSR. 176:1:124 (1967)
11. L.Pakett. Principle of modern chemistry of heterocyclic compounds. Mir, Moscow, 1971, p. 220
12. Haake P., Mantegon J. J. Am. Chem. Soc. 86: 5230 (1964)
13. Vorobiev P.B., Saurambaeva L.I., Gabdrakipov V.Z., Neverdovsky G.G., Sembaev D.Kh. Izvestiya MON RK, NAN RK. Ser. Khim 5:97 (2000).

Received 4 May 2003.

D.Kh. Sembaev et al.

Eurasian ChemTech Journal 6 (2004) 127-131