

Materials of Conferences

**DEVELOPMENT OF METHOD
OBTAINING M-XYLYLENDIAMINE
FOR PRODUCTION OF POLYMERIC
MATERIALS**

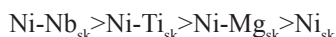
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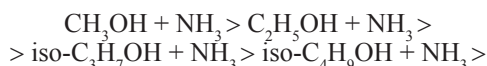
The results of studying reaction of isophthalonitrile hydration upon promoted catalysts at the foundation of Ni-Rhenejais alloy Ni:Al = 1:1 in spirit environment under the pressure of oxygen in presence of ammonia.

It is established that in the described conditions studied catalysts can be placed in the following line according to degradation of isophthalonitrile hydration:



And according to output of m-xylylenediamine (m-XDA) sequence of catalysts preserves. Alloying of Ni-Al-alloy with a small amount of Ti, Nb has a positive effect upon activity and selectivity. Activity of Ni-Nb_{sk} catalyst in 2–3 times greater than that of Ni-Ti_{sk} and Ni-Mg_{sk}, and 4–5 times greater than that of Ni_{sk}.

It is shown that the studied solvents can be placed in the following line according to degradation isophthalonitrile hydration speed on Ni-Nb_{sk} under 4,0 MPa of H₂ and 80 °C:



In aliphatic spirits (C₁-C₄), under nitrile-ammonia proportion = 1–3 (g/g), output of XDA equals 96–98% on Ni-Nb_{sk} catalyst.

Nowadays attention of researchers is mostly drawn to problems of using lipid-aromatic diamines in synthesis of heat-resistant polymers, as introduction of aromatic rings into the chain of polymers increases solidity of thermomolecula, temperature of softening and melting sharply [1]. The basic similar product for heat-resistant polymers will be m-, p-xylylenediamines, synthesized via catalyst hydration of isophthalo- and terephthalonitriles, received via oxidation ammonolysis of m-, p-xylois [1, 2]. Therefore, problem of synthesizing m-, p-xylylenediamines draws our interest for studying.

The most rational method of receiving m-xylylenediamine is catalyst hydration of isophthalodinitrile, received via oxidation ammonolysis of oil m-xylois. Up until the modern days kinetics and mechanisms of hydration isophthalodinitrile into m-xylylenediamine are not studied sufficiently.

The objective of this work is to develop an efficient method of receiving m-xylylenediamine,

monomer for heat-resistant polymers, via hydrating isophthalonitrile.

Earlier all researches, devoted to a direct hydration of isophthalo-, terephthalonitriles were carried out in static conditions, and consumption of hydrogen was monitored according to a drop of hydrogen pressure in the system. Among such researches we can outline works by academy member A.A. Balandin, L.K. Freindlin, T.A. Sladkova, and others [3, 4] and academy member D.V. Sokolskiy, F.B. Bazhanov [5]. Among the disadvantages of these works we can outline lack of studies on kinetics of nitrile group hydration, hard conditions of the process, and insufficient output of the desired product ($P_{\text{H}_2} = 10,0\text{--}20,0$ MPa H₂, $T = 120\text{--}150$ °C, output of m-, p-xylylenediamine 80–90%).

The work [6] describes catalyst method of receiving m-xylylenediamine from isophthalonitrile on Ni / fossil meal under 80–100 °C, 8,0 MPa H₂ in presence of organic solvent and ammonia (mole proportion of isophthalonitrile:dioxane:ammonia = 1:3:2). Output of m-xylylenediamine equals 80–85%.

The author's testimony [7] describes catalyst method of receiving m-, p-xylylenediamine from isophthalo-, terephthalonitriles on Pt-Ni / Al₂O₃ or Pd-Ni / Al₂O₃ under 120–130 °C, 22,0 MPa H₂ in presence of organic solvent (xylois, toluol, propanol) and ammonia (mole proportion of isophthalonitrile/ammonia = 1:50–100). Output of m-, p-xylylenediamine 90–95%. For disadvantages of this method we can outline hard conditions of the process on noble metals in presence of great amount of ammonia.

In industry m-xylylenediamine is received via electrochemical restoration of isophthalonitrile, its catalyst hydration on Ni-Rheneja, Pt, or Pd / Al₂O₃ (60–100 °C, 10,0–13,0 MPa H₂) in organic solvents leads to cyanbensilamine.

Materials and methods of research. With the aim of intensifying the catalytic synthesis of m-xylylenediamine isophthalonitrile for the first time we studied in the presence of various alloyed catalysts based on Ni-Raney, showed high activity and selectivity in hydrogenation reactions of other aromatic compounds.

Catalytic hydrogenation of isophthalonitrile was conducted in the liquid phase in the isobaric-isothermal mode to a high-pressure kinetic (KUVD) allowing monitoring the consumption of hydrogen per unit time [8]. The reactor is a catalytic “duck” stainless steel. The volume of the reaction vessel is 0,15 l., the number of single-sided swing of 600–700 per minute. Solvent – alcohol + NH₃. Hydrogenation is carried out until the termination of hydrogen uptake from the gas phase. The equipment and the experimental procedure described previously [9], the catalyst is prepared according to known methods [5].

For the analysis of hydrogenation products were applied potentiometric titration, IKS, Fourier-spectroscopy and elemental analysis.

Results of research and their discussion. In the study of catalytic hydrogenation isophthalonitrile we deliberately were trying to select such process conditions – the catalyst, solvent, temperature, hydrogen pressure, and the ratio of ammonia to dinitrile, which could provide a high yield and quality of the desired product while reducing the duration of the experiment.

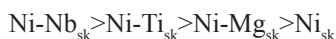
Comparative results for the hydrogenation of isophthalonitrile Ni-Reneyaz Ni-alloy Ni: Al = 50:50 and modified with additives Mg, Ti, Nb catalysts based on Ni-Raney in ethanol at 4,0MPa H₂ pressure and 80 °C show that a characteristic feature of the kinetics of the hydrogenation of isophthalonitrile as in the case of the hydrogenation terephthalonitrile it is constant and fairly large (for large initial velocities) reducing the reaction rate throughout the experiment [1, 10].

On the Ni-Raney (Ni_{sk}), a fairly sharp decrease in the rate of hydrogenation, and by the time hemihydrogenation (after absorption of 2,0 moles (50%) of the desired hydrogen) it becomes zero, that is, reaction dies, apparently as a result of the formation of byproducts.

On the catalysts Ni-Mg_{sk}, Ni-Ti_{sk} and Ni-Nb_{sk} hydrogenation rate of izoftalonitrile hemihydrogenation becomes an order of magnitude lower than the original; the test was terminated by absorption of the calculated amount of hydrogen. By active catalyst Ni-Nb_{sk} turned is 5 times as active Ni_{sk} and Ni-Mg_{sk}, Ni-Ti_{sk} - almost 2–3 times.

It has been established that catalysts Ni-Mg_{sk}, Ni-Ti_{sk} and Ni-Nb_{sk} izftalonitrila hydrogenation proceeds at a decreasing rate with time, the calculated amount of hydrogen is absorbed. The hydrogenation starts with a very high rate of absorption to two moles of hydrogen per mole of dinitrile, after which the rate of hydrogen absorption decreases somewhat, the next two moles of hydrogen are joined slowly.

Hydrogenation of izoftalonitrile to m-xylylenediamine in a liquid phase under a hydrogen pressure of isobaric-isothermal conditions investigated to reduce the activity of catalysts arranged in series:

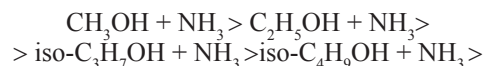


We have previously shown that the hydrogenation terephthalonitrile significant influence on the process by the nature of the solvent, and the best results are achieved when using alcohols in the presence of ammonia [1, 10]. Solubility of phthalonitriles, e.g., methanol at 25 °C in order to increase the presence of ammonia in comparison with pure methanol, and the temperature rises to 50 °C for a further two times.

We are in our studies under the hydrogenation of izoftalonitrile to m-xylylenediamine for the cata-

lyst Ni-Nb_{sk} in liquid phase under a hydrogen pressure of isobaric-isothermal conditions (4,0 MPa H₂, at 80 C) was used as solvent, methanol, ethanol, isopropanol previously saturated with ammonia under cooling (nitrile: ammonia = 1: 1 and 1: 3 ratio in g).

It was shown that the investigated solvents to reduce the rate of hydrogenation of izoftalonitrile arranged in the following series:



The output from m-xylylenediamine (m-CDA), the sequence arrangement of solvents is maintained. The shape of the kinetic curves does not change.

Suitable ratio of the reactants on the catalyst surface in alcohol in our experiments is observed at a ratio of nitrile: ammonia = 1:3 (g / g). In the alcohol in a ratio of nitrile: ammonia = 1: 3 (g / g), the yield of m-CDA on Ni_{sk} 68–70% on Ni-Mg_{sk}, Ni-Ni-Ti_{sk} and Nb_{sk} catalysts 90–91, 91–92 and 96–98% respectively.

From this sequence, it follows that as the molecular weight increases the rate of hydrogenation of izoftalonitrile alcohol in a solvent decreases.

Increasing the speed of hydrogenation and high yield of m-xylylenediamine (96–98%) in the alcohol-ammonia solutions favors aldiminovo mechanism [1, 3, 5, 9–14].

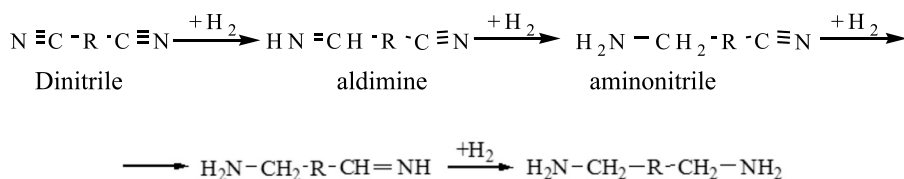
To confirm the completeness of the reaction hydrogenation of izoftalonitrile to m-xylylenediamine, we studied the infrared spectra of the final product to catalytic reduction izoftalonitrile-promoted the skeletal catalyst Ni-Nb_{sk}.

The final product (after the absorption of 4.0 moles of hydrogen required) in the IR spectrum the absorption bands disappear completely, corresponding S≡N group (valency fluctuations 2240–2230 cm⁻¹), and in 3400–3290 cm⁻¹ manifested intense absorption bands of stretching vibrations of the NH₂ group [9, 10, 15].

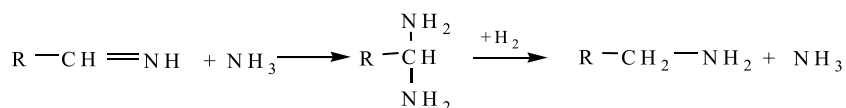
The desired product m-xylylenediamine – a colorless liquid; temp. Solidification 14 °C. temp. boiling. 245–248 °C, 105 °C / 2 mm Hg.; d₄²⁰ 1,055; n_D²⁰ 1,5720. It is readily soluble in ether, dioxane, and lower aliphatic alcohols.

FT-IR and Raman spectra of the starting materials and reaction products were recorded on FTIR spectrometer IFS-66 with Raman prefix FRA-106.

The formation of the aminonitrile in the catalytic hydrogenation of aromatic dinitriles indicates sequential recovery of the nitrile groups [1, 5, 10, 12]. First intermediate compound formed on the surface of the catalyst in the hydrogenation of nitriles and dinitriles is aldimine [1, 3, 5, 9–14]:



The classic way of getting primary mono- and diamines is hydrogenation process of nitriles and dinitrils in the presence of ammonia [1, 3–7, 9–12]. Ammonia prevents reactive aldimines react with a primary amine, which are formed by reacting a Schiff base and further reaction with hydrogen pass-

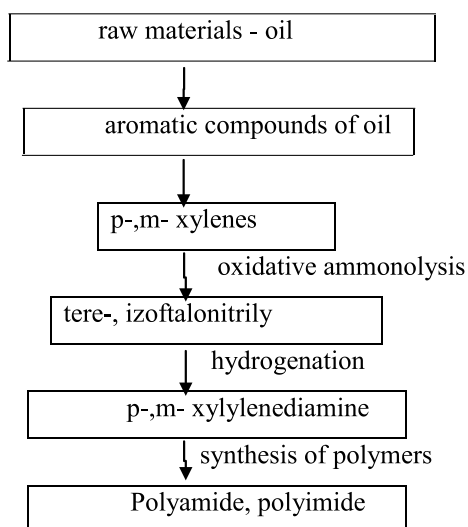


To direct the reaction towards the formation of primary mono- and diamines is necessary to increase the hydrogen concentration on the catalyst surface, for example, using elevated hydrogen pressure and strengthen the adsorption of hydrogen bond with the surface by promoting the skeletal nickel, or the selection of the solvent, in particular, its introduction into the ammonia or additives basic character [1, 3–7, 9–12, 16, 17].

Many authors attributed the increased activity of skeletal Ni-Ti_{sk}, and Ni-catalysts Nb_{sk} to a change ratio NiAl₃ aluminide alloy and Ni₂Al₃ in upward phase NiAl₃, which leads to a change in the lattice parameters Ni. The observed deformation of the lattice of nickel is an additional indication in explaining the higher activity of the catalyst. The activity and selectivity of studied catalysts under the catalytic synthesis of primary amines can be associated with a high degree of enrichment of the catalyst strongly bound by adsorbed hydrogen and the oxides of d-metal oxide catalysts in skeletal layer leads to an increase in the proportion of micropores, increase in the specific surface of the catalyst influence the adsorption properties, selectivity and stability.

Introduction to the Ni-Al-alloy and oxidize easily leachable infusion (up to 10 wt. %), leads to an increase in efficiency factor [1, 10, 16, 17].

General Linear flowsheet producing polymers can be represented as follows:



es to a secondary amine. It is also possible interaction with a secondary amine aldimine [5, 9–13]. A reactive aldimine interacting with ammonia forms an unstable compound, which is easily transferred to the primary amine, by interacting with the hydrogen and splitting off the ammonia [1, 5, 9, 10, 12]:

The authors of [1] terephthalonitrile synthesized by hydrogenation of p-xylylenediamine, and on its basis – heat-resistant polymers.

Conclusion. Experiments with a high-pressure kinetic showed that under the conditions of the experiment on Ni-promoted Mg_{sk}, Ni-Ti_{sk}, Ni-Nb_{sk} catalyzators the liquid phase hydrogenation proceeds at a decreasing rate over time. The hydrogenation starts with a very high rate of absorption to two moles of hydrogen per mole of dinitrile, after which the rate of hydrogen absorption decreases somewhat, the next two moles of hydrogen are joined slowly.

The activity of the catalyst Ni-Nb_{sk} in 2–3 times higher than Ni-Ti_{sk} and Ni-Mg_{sk} and 4–5 times higher activity of Ni-Raney (Ni_{sk}).

It is shown that the experimental conditions studied (4,0 MPaN₂ and 80 °C) with increasing molecular weight of the alcohol rate of hydrogenation in a solvent izoftalonitrile is decreasing. The form of the kinetic curves is being unchanged. The aliphatic alcohols (C₁-C₄) at a ratio of nitrile: ammonia = 1: 3 (g / g), the yield of m-xylylenediamine is on Ni-catalyst Nb_{sk} 96–98%.

An attempt was made to explain the course of the process of catalytic hydrogenation of izoftalonitrile to m-xylylenediamine by aldimine mechanism.

General linear flowsheet producing polymers can be represented as follows: Raw material – Oil → Aromatic compounds of oil → p, m-xylene → tereftalo-, izoftalonitrily → p, m-xylylenediamine → polymers.

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The work is submitted to the International Scientific Conference “Engineering science and modern manufacture”, France, October, 18–25, 2015, came to the editorial office on 28.07.2015.

SPACE MONITORING OF MAN-MADE HAZARDS IN CENTRAL KAZAKHSTAN

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In article features of data processing of space monitoring of territories with the purpose of prevention of technogenic emergencies are considered. Here is the interferogram, settling in the region of Karaganda region.

Space monitoring is the continuous multiple getting information about qualitative and quantitative characteristics of natural and man-made objects and processes with the exact geographical position at the expense of processing the data received from the satellites, Earth remote sensing (ERS). Space monitoring allows to obtain uniform and comparable quality information at a time for vast territories, which is al-

most unattainable for any of ground surveys. Based on this definition, we can distinguish a number of basic requirements to space monitoring: the ability to monitor large areas and long features; high spatial resolution (up to 50 cm) and precision, including without ground anchor points; high frequency of surveys, the efficiency of obtaining the original and processed RS data; the possibility of building digital elevation models (DEM) and of localities on the stereo images from the SPACECRAFT (SC) remote sensing; the ability to take the picture in a large number of spectral channels; possibility of use of materials of space monitoring directly in all standard GIS.

Operational space monitoring of natural and technogenic emergencies and disasters in recent years has become the most important and necessary component of information provision services respond to emergencies. Every day we receive space data is widely used for providing information for audit and predictive models security areas and hazardous production facilities. Using the modern GIS-technologies, allowing to unite the diverse information with space data. This allows you to automate the calculations of the risk of disaster (fires, droughts, floods etc). Possibilities of space monitoring zones of emergency from space are determined by the availability of imagery, spatial resolution of observed objects, availability of images.

Data processing of remote sensing – the process of the operations of aerospace images, including their correction, transformation and improvement, interpretation, visualization.

The main stages of space images processing: the preliminary processing, the thematic.

Preliminary processing of multispectral data is the correction and improvement of satellite images.

The pre-processing includes the geometric correction of satellite images, the radiometric calibration of images, the radiometric correction of influence of the atmosphere, the restoration of the missing pixels, the contrasting, the filtering. Geometric correction includes the elimination of the image geometric distortion (orthorectification), the geographical location.

Photos, originally received from satellites that have been recorded in the so-called “raw values” brightness DN (Digital Number). The data in this format cannot adequately be compared with the data of other surveys. The task radiometric calibration is adjusting these values in physical units.

Image contrast is the difference between the maximum and minimum values of brightness.

Weak contrast – the most widespread defect images.

Filtering is a transformation that allows you to enhance the reproduction of certain objects, suppress unwanted veiling, to resolve other random interference (noise). The essence of objects is useful to define at the image in natural colors, but to share and delineate objects easier on the image in false colors. Choosing the right scale allows the