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INFLUENCE OF NANOSTRUCTURAL CATALYST IN THE SYNTHESIS OF ALLYL PHENYL ETHER AND OF IT'S ISOMERIZATION PRODUCTS

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Attention to 2-allylphenol (2-AF) and its synthesis is due by the fact that this compound is the starting material for the production of a number of biologically active natural compounds, such as synthetic fungicide. A number of recent publications have shown the high activity of zeolite, rhodium, iridium, and ruthenium catalysts in allylation reactions. The lack of these catalysts is their high cost. Therefore, the use of new effective and inexpensive catalysts in the reactions of synthesis and isomerization of allyl phenyl ether is important problem.

The aim of this work is the selective synthesis of *o*-allylphenols in the isomerization of allyl phenyl ether under mild conditions using nanostructured catalysts. The methodology of the work is in finding new available and effective catalysts for the synthesis and targeted isomerization of allyl phenyl ether. When using nanostructured catalysts in the reaction of isomerization of allyl phenyl ether, using a mass chromatography method, it was found that the products of isomerization of allyl phenyl ether for one hour at a temperature of 90-95 °C are: (56%) 2-allylphenol; (2%) *p*-allylphenol, (12%) allyl-*o*-allyl phenyl ether, (4%) allyl-*p*-allyl-phenyl ether, and (26%) unisomerized allyl phenyl ether. For the first time the possibility of using small amounts of nanostructured catalyst Fe/SiO₂:TiO₂ in the synthesis of allyl phenyl ether and of its isomerisation products has been shown.

Keywords: Fe/SiO₂:TiO₂ nanocatalyst, allyl phenyl ether, a mixture of ortho and para-allyl phenols, chromato-mass spectroscopy, rearrangement

ВЛИЯНИЕ НАНОСТРУКТУРНОГО КАТАЛИЗАТОРА НА СИНТЕЗ АЛЛИЛФЕНИЛОВОГО ЭФИРА И ПРОДУКТОВ ЕГО ИЗОМЕРИЗАЦИИ

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Интерес к 2-аллилфенолу (2-AF) и его синтезу объясняется тем, что это соединение является исходным материалом для получения ряда биологически активных природных соединений, таких как синтетический фунгицид. Ряд недавних публикаций показал высокую активность цеолитных, родиевых, иридиевых и рутениевых катализаторов в реакциях аллилирования. Но недостатком этих катализаторов является их высокая стоимость. Поэтому использование новых эффективных и недорогих катализаторов в реакциях синтеза и изомеризации аллилфенилового эфира является важной задачей.

Целью данной работы является селективный синтез *o*-аллилфенолов при изомеризации аллилфенилового эфира в мягких условиях с использованием наноструктурированных катализаторов. Методология работы заключается в поиске новых доступных и эффективных катализаторов для синтеза и целевой изомеризации аллилфенилового эфира. При использовании наноструктурированных катализаторов в реакции изомеризации аллилфенилового эфира, с использованием метода массовой хроматографии, было обнаружено, что продуктами изомеризации аллилфенилового эфира в течение одного часа при температуре 90-95 °C являются: (56%) 2-аллилфенол; (2%) *p*-аллилфенол, (12%) аллил-*o*-аллилфениловый эфир, (4%) аллил-*p*-аллилфениловый эфир и (26%) неизомеризованный аллилфениловый эфир. Впервые показана возможность использования небольших количеств наноструктурированного катализатора Fe / SiO₂:TiO₂ при синтезе аллилфенилового эфира и продуктов его изомеризации.

Ключевые слова: нанокатализатор Fe / SiO₂:TiO₂, аллилфениловый эфир, смесь орто- и пара-аллилфенолов, хромато-масс спектроскопия, перегруппировка

ALLILFENIL EFIRI VA UNING ISOMERIZATSIYA MAHSULOTLARINI SINTEZ QILISHDA NANOSTRUKTURALI KATALIZATORNING TA'SIRI

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2-Alilfenolga (2-AF) va uning sinteziga e'tibor, bu birikmalar tabiiy biologik faol birikmalar ishlab chiqarish uchun boshlang'ich material va sintetik fungitsid vositasi ekanligi bilan izohlanadi. So'nggi yillarda nashr etilgan bir qator ishlarda zeolit, rodiiy, iridiiy va ruteniiy katalizatorlarining allilash reaksiyalarida yuqori faolligini ko'rsatdi, ammo ularning noqulayligi ularning yuqori narxidir. Shuning uchun allilfenil efrining sintezi va izomerizatsiyasi reaksiyalarida yangi samarali va arzon katalizatorlardan foydalanish dolzarb muammo hisoblanadi.

Ushbu ishning maqsadi nanotuzilishli katalizator yordamida yumshoq sharoitlarda allilfenil efrining izomerizatsiyasida *o*-alil fenollarni tanlab sintez qilishdir. Ushbu allil fenil efrini sintez qilish va izomerizatsiya qilish maqsadida yangi mavjud va samarali katalizatorlarni qidirishdan iborat. Allilfenil efrining izomerizatsiya reaksiyasida nanotuzilishli katalizatorlardan foydalanishda uning izomerizatsiyasi 90-95 °C haroratida bir soat davomida olib borilganda aralashma tarkibi xromato-mas spektrometriya yordamida quyidagilar ekanligi aniqlandi: (56%) 2-allilfenol; (2%) *p*-allilfenol, (12%) allil-*o*-allilfenil efir, (4%) allil-*p*-allilfenil efir va (26%) izomerlanmagan allilfenil efir. Allilfenil efir va uning izomerizatsiyasi mahsulotlarini sintez qilishda oz miqdordagi Fe/SiO₂:TiO₂ nanotuzilishli katalizatoridan foydalanish imkoniyati birinchi marta ko'rsatildi.

Kalit so'zlar: Fe/SiO₂:TiO₂ nanokatalizatori, allilfenil efir, orto- va para-allilfenollarning aralashmasi, xromato-mas spektroskopiya, qayta guruhlanish

Introduction

Allyl phenyl ethers and allylphenols obtained as a result of its rearrangement are found practical application in various industries. They are used as compounds introducing are in composition of vitamins, herbicides, fungicides, inhibitors of microbiological corrosion of metals, as intermediates for the production of drugs, dyes and inhibitors of thermal oxidative degradation of polymers [1]. Attention to 2-allylphenol (2-AF) and its synthesis is due by the fact that this compound is the starting material for the production of a number of biologically active natural com-

pounds. In addition, 2-allyl phenol is currently actively used as a precursor or starting compound for the synthesis of monomers in the creation of bismaleimide resins with high mechanical characteristics, thermal stability, and corrosion resistance [2]. 2-Allylphenol is an effective fungicide against a number of phytopathogens. It effectively controls various fungal diseases of plants such as stem rot in apple tree (*Valsamali*), gray tomato mold (*Botrytis cinerea*), spotting of maize leaves (*Drechslerterracea*), rizoktoniosis (spots on wheat leaves) (*Rhizoctonia cerealis*) and powdery mildew (*Sphyrnophyta tubercica*). It is

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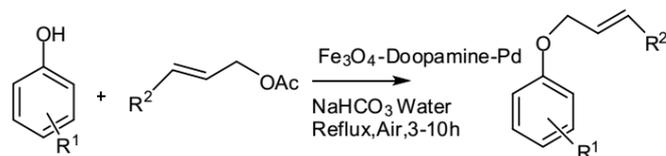
also the main component in the synthesis of bi-functional benzoxazines, which activate the germination of wheat seeds and exhibited growth-regulating and anti-stress activity [3].

Allyl phenyl ether is an intermediate at synthesis of metabolites: diclofenac and nonsteroidal (didn't-steroidal anti-inflammatory drugs) [4].

Recently interest to elaboration development of catalytically active porous metal oxides lies in obtaine uniform pore size of mesoporous materials (2-10 nm), which have allowed spatially hindered molecules to easily diffuse into internal active regions. The general synthesis of mesoporous metal oxides with large porouses in a semi-crystalline structure, including mesostructured $\text{SiO}_2 \cdot \text{TiO}_2$, is described in detail in [5–7].

A number of recent publicated works have been shown the high activity of zeolite catalysts in alkylation reactions [8]. The use of natural zeolite, clinoptilolite and mordenite, has been investigated [9]. The proposed method for their production has more advantages in comparison with traditional ones: high selectivity, less in material and energy resources. Allyl phenyl ether was synthesized by intereaction of allyl alcohol with phenol (molar ratio = 1:1) in the presence of zeolite and hydroquinone (0.5 g per 0.5 mol of allyl alcohol). Allyl alcohol was introduced into a flask with a dried phenol complex on zeolites. The temperature of the reaction medium was to 250-300 °C. The reaction products were removed with diethyl ether and dried over MgSO_4 . The obtained substances were analyzed by gas-liquid chromatography, and thin layer chromatography (TLC). The phenol alkylation with allyl bromide was previously studied with aim of selective synthesize of allyl phenyl ether in conditions of interphase catalysis (MPC) [9]. Depending on the reaction conditions along with the desired allyl phenyl ether, o-allylphenol, p-allylphenol were obtained, as well as small amounts of diallyl ether (owing to hydrolysis of allyl bromide to allyl alcohol and its further alkylation), as well as (o-allyl) phenol and (p-allyl) phenol. In reactions in the presence of MPA allyl phenyl ether was formed with more yield (56%) compared with the reaction without catalyst 12%. It was noted that the composition of phenol allylation products depends on the pore size of zeolites. A mixture of allylated phenols was obtained with yield of 80%. It is known that at temperatures below 600 K the zeolite surface is coated with phenol, which forms a complex with the surface. In this case the formation allyl phenyl ether also was observed. It has been found that allyl phenols form at temperatures above 400 °C. Heating the allyl phenyl ether in conditions of the alkylation reaction leads to the formation of allylphenols with low yield. The yield of C-allylphenol has increases with increasing reaction temperature.

One of the methods producing allyl phenyl ethers, in the framework of alternative sustainable technologies of green chemistry, is the allylation with using magnetically extractable catalysts. Thus, allyl ethers in water were synthesized by O-alkylation of phenols by allylacetates in the presence of a magnetically extractable heterogeneous Pd catalyst [10].



Thus, the using of this catalyst in result of its simple extraction using an external magnet, high stability and efficient recirculation, has been contributed to production of economical and stable allyl phenyl ethers. In the work of Wuand Lo [11] was shown that the quaternary ammonium membrane can be used as an effective interfacial catalyst for allylation of phenol in a membrane reactor. Today, ion-exchange membranes are the most advanced separation membranes. They are successfully used in the desalination of sea water, the recovery of metal ions from wastewater, and electro dialysis experiments. The reaction system selected for further investigations consisted from allyl bromide and phenol, with a quaternary ammonium salt deposited on the membrane as a three-phase catalyst in an organic solvent or alkaline solution. Two types of anion-exchange membranes (TMA, A172) with different functional groups of tert-amines were obtained by the reaction of a membrane copolymer consisting from chlormethylstyrene and divinylstyrene with various amines (trimethylamine and tri-n-butylamine). The study showed that the TMA and A172 membranes can be properly used as a catalyst increasing the reaction ability of phenol allylation [12].

In this regard, systematic investigations by production of allyl ethers and allyl phenols with using of nanostructured catalytic systems are actual fundamental problem.

Material and methods

Tetraethylorthosilicate (TEOS, Shin-Etsu Chemical Chemical.) was used as a source of silica. Titanium isopropoxide (TIPT, $\text{Ti}(\text{OiPr})_4$), tetrabutyl titanate (TBT, $\text{Ti}(\text{OBu})_4$), titanium tetrachloride (TiCl_4) or a 30% solution of titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) were used as sources of titanium. Acetylacetonate (acac) was used as a chemical modifier to control the reactivity of TIPT. Poly(ethylene glycol) (PEG) with an average molecular weight of 20,000 was used as the polymer component to induce phase separation. Aqueous solutions of 60% nitric acid (HNO_3) and 35% hydrochloric acid (HCl) were used as hydrolysis and polycondensation catalysts.

All chemicals except TEOS were purchased from Wako Pure Chemical Industries, Ltd. They were used without further purification.

Synthesis Procedures

Titanium dioxide-silica samples were prepared using several mixing methods of mixing to control the dispersion of Ti in a SiO₂ network [14]. At preparing samples with using titanium isopropoxide (TIPT) as a precursor to titanium dioxide, the co-gelation method was used. At which, the required amount of polyethylene glycol (PEG) with an average molecular mass 20,000 was dissolved in aqueous solution of nitric acid. In another vessel tetraethylorthosilicate (TEOS) and TIPT were mixed. The PEG solution was poured into an alkoxides mixture at stirring in cooling ice bath. A homogeneous solution is obtained after stirring for several minutes, which matured at 25,30 or 50 °C for 1 day. After that, the gels were left at 50 °C for 1 week to dry. The dried gels were calcined at 600 or 900 °C. The titanium dioxide content was on level 7,6 mass.%.

Synthesis of allyl phenyl ether

In a three-necked round-bottom flask connected with stirrer, a dropping funnel and a reflux condenser, sodium alcohol solution of phenol phenate is poured and allyl bromide was introduced at working stirrer (molar ratio of sodium phenolate to allyl bromide = 1:1). The dropping funnel was replaced by thermometer, the reaction mixture was heated during 1 hour in a water bath at temperature of 70-80 °C. A white precipitate of NaBr is formed as a result of the reaction. The reaction products were identified by TLC (thin layer chromatography) with one spot with R_f = 0,783, what has corresponded to the R_f value of allyl phenyl ether. After cooling the reaction mixture, the precipitate was filtered. Ethyl alcohol was distilled from the filtrate under ordinary conditions; then, allyl phenyl ether was isolated by fractional distillation under vacuum. The reaction yield was 81%. In order to determine the composition of the products chromatography-mass spectrometry was performed. The analysis shown that the obtained mixture has contained: 78% allyl phenyl ether, 12% 2-allyl phenol. A thin-layer chromatography plate (TLC) DC-Fertigfolien ALUGRAM® Xtra SIL G/UV₂₅₄ (Germany) were used, the appearance of spots was determined under the action of UV lamp on the plates. Solvent system benzene: ethyl acetate (3:1).

The reaction products were identified by method IR (Perkin Elmer Spertum IR, Version 10.06.1) and NMR H¹ and ¹³C (Unity 400 plus ICPSASR Uz, Si(CH₃)₄ standard) Solvent C₆D₆. For chromatography-mass spectrometry, MassHunter/GCMS/1/597 instruments (Agilent

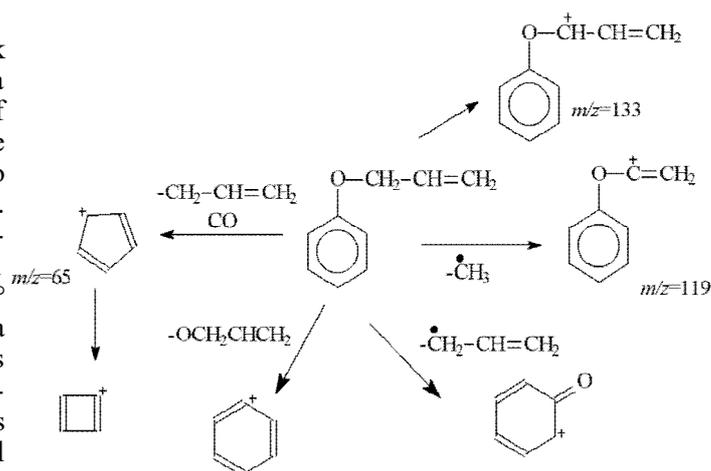
technologies) were used.

Allyl phenyl ether bp = 192 °C; in vacuum T_p = 115 °C, d₄²⁰ = 1.5223, R_f = 0,783, n_D²⁰ = 1,5207, IR spectra (KBr, cm⁻¹), 682-750 (monosubstituted benzene), 923-990 (-CH=CH₂), 1219-1240 (asymmetric stretching vibrations of the bond C-O-C-), 1031,85 (symmetrical stretching vibrations of the bond C-O-C), 3040,88 (C-H bonds in the aromatic ring), 1494, 1586, 1598 (-C-C- in the aromatic ring).

NMR H¹ (Unity 400 plus ICPSASR Uz, Si (CH₃)₄ standard) Solvent C₆D₆; chemical proton shift) δ 6,7 (d, 2H, ArH) and 7,1 (t, 3H, ArH), 4,05 (m 2H, O-CH₂), 4,8 va 5,1 (m, 2H, =CH₂), 5,7 (m, 1H = CH).

¹³C spectrum (100 MHz, C₆D₆) d = 35,18; 68,92; 115,38; 116,19; 117,37; 121,19; 128,39; 130,05; 134,13.

For chromatography-mass spectrometry MassHunter/GCMS/1/597 instruments were used. Agilent technologies. Fragmented mass-spectrum ions with m/z C₉H₁₀O is shown below:



Preparation of Nanocatalyst

The Fe/SiO₂·TiO₂ catalytic system was prepared by following method: FeCl₃·6H₂O and SiO₂·TiO₂ were weighed in amount of 2·10⁻⁴ grams on analytical balance. Nanocatalyst powder was added to dissolved in 2 ml of FeCl₃·6H₂O water. The obtained system was heated at stirring, then has been dried at a temperature of 120 °C.

Allyl phenyl Ether Isomerization Reactions

The reaction was carried out in a three-neck round-bottomed flask with a capacity of 250 ml. The flask was connected which thermometer and a reflux condenser closed by a calcium chloride tube. A 6 ml of allyl phenyl ether solution was poured, in solution 2·10⁻⁴ mol SiO₂·TiO₂·FeCl₃·6H₂O. Within an hour the mixture is heated at temperature 90-95 °C. The second spot was identified by TLC, the R_f value of which has corresponded to o-allylphenol (R_f = 0,55). A comparison of IR spectroscopy of a mix-

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Table 1

The results of the analysis of the synthesis products of allyl phenyl ether by gas chromato-mass spectroscopy

Retention time	Peak area	Concentration, %	Substance
3,571	38101630	3,841253	Phenol
4,247	777644661	78,399	Allyl phenylether
4,784	120396210	12,13786	2-Allylphenol
5,042	6015321	0,60644	p-Allylphenol
5,324	23825500	2,401991	Allyl (o-allyl) phenyl ether
5,57	20096911	2,026089	Allyl (p-allyl) phenyl ether

ture of allyl phenyl ether and its isomerization product has confirmed carrying with the reaction and the formation of o-allyl phenol. The composition of the mixture products was determined by chromato-mass spectroscopy: o-allyl phenol (56,39%), ether (20,89%) and p-allylphenol (1,54%).

o-Allylphenol bp = 220 °C, in vacuum bp = 134 °C, $R_f = 0,55$.

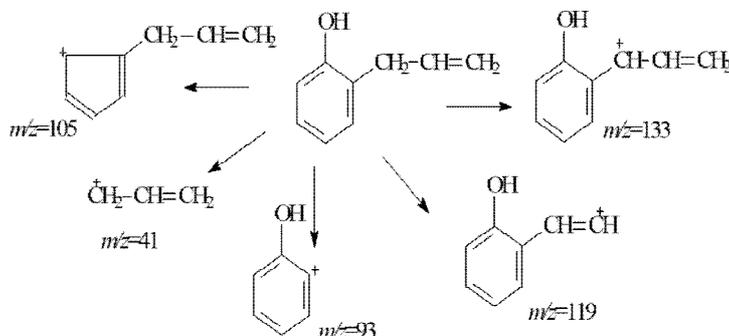
p-Allylphenol bp = 238 °C, in vacuum bp = 137 °C, $R_f = 0,417$.

IR spectra (KBr, cm^{-1}) show intense stretching vibrations of the —OH 3436,32 group and deformation vibrations of the —OH group at 1329,17. stretching vibrations of the CH bond in the aromatic ring 3040,88, 1638,20-1597,25 ortho C-C bond in the aromatic ring.

Analysis of the PMR spectrum: (400 MHz, C_6D_6 , chemical shift of protons (δ , ppm)). Doublet protons of the aromatic ring are shown in 6,5 and 7,0 ppm. (2H, ArH), triplet at 6,7 and 6,87 ppm. Protons of the methylene group attached to the aromatic ring are detected by multiplet signals at 3,2 ppm. (2H, $-\text{CH}_2-$). 5–5,2 ppm (m, 2H, = CH_2). The proton of the hydroxyl group is marked by a signal in 5,44 ppm.

Spectrum ^{13}C (100 MHz, C_6D_6), $d = 35,14$; 115,45; 116,15; 121,46; 126,64; 128,22; 131,06; 137,19; 154,58 ppm.

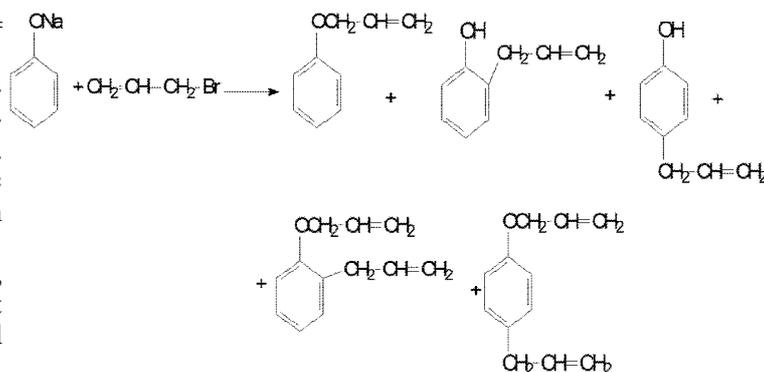
Fragmented mass spectrum ions: m/z $\text{C}_9\text{H}_{10}\text{O}$: 134, 133, 119, 115, 107, 105, 98, 77, 79, 51:



Results and discussion

The initial stage in the synthesis of allyl phenyl ether was the production of sodium

phenolate by dissolving sodium in absolute alcohol and adding phenol in calculated amounts. A reaction was carried out by reacting the obtained sodium phenolate with allyl bromide. The reaction of sodium phenolate with allyl bromide in solution of ethyl alcohol proceeds easily with formation of crystals of sodium bromide with yield of 90%:



For determination of the composition of the mixture products chromato-mass spectroscopy was used (Table 1).

Allyl phenyl ether was purified from allylphenol impurities by washing benzene solution of the mixture Kleisen alkali, and the residue after drying was distilled in vacuum. Chromatographically pure allyl phenyl ether was obtained.

Allyl phenyl ether isomerization can be carried out with using of various catalysts. The use of acid catalysts in the isomerization reaction has accelerated reaction of polyallylation and polymerization of olefins.

The rearrangement of allyl phenyl ether in the presence of small amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was accompanied by the predominant formation of allylphenol [13], what significantly has complicated the directed synthesis of o- and p-allylphenols. In the reaction of phenol (with excess) with allyl acetate small amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (molar ratio phenol:allyl acetate: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = 5:1:4 \cdot 10^{-4}$) were used as a catalyst at a temperature of 74–75 °C for 5 hours, allyl phenyl ether, 2- and 4-allyl phenols have been formed. Determine of composition of the

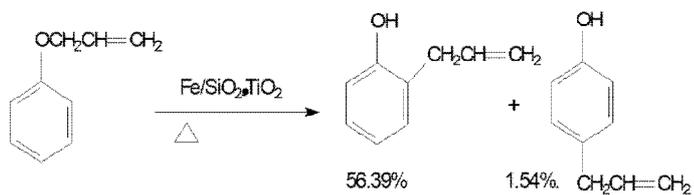
Table 2

The results of the products of isomerization of allyl phenyl ether by the analysis of chromato-mass spectroscopy

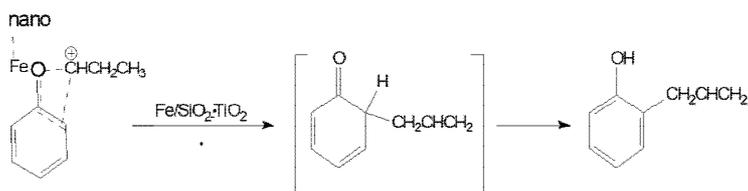
Retention time	Peak area	Concentration, %	Substance
4,204	110572411	20,89	Allyl phenyl ether
4,835	298420199	56,39	2-allylphenol
5,059	8150133	1,54	4-allylphenol
5,35	62863728	11,88	Allyl(2-allyl)phenyl ether
5,586	15217695	2,88	Allyl(4-allyl)phenyl ether

reaction products in the analyzed mixture was performed (by using GLC Rxi-624SilMS instrument of Restek, USA company. GLC conditions: column length 30 m, with inner diameter 0,25 mm, column temperature - 200 °C, temperature injector - 220 °C, temperature FID1-220 °C, $V_{N_2} = 50$ ml/min). The analysis of the sample has showed following contents of components (%): Allyl phenyl ether - 43,3; o-allyl phenol - 16,3; p-allylphenol-40,4.

Therefore, the allyl phenyl isomerization reaction was carried out in the presence of small amounts of the new $Fe/SiO_2 \cdot TiO_2$ nanocatalyst which not previously wasn't used and described in the literature. The rearrangement reaction scheme is shown below:



The rearrangement mechanism can be explained by formation of a cyclic transition state:



The duration of the reaction was determined by TLC with an interval of half hour in solvent system benzene:ethyl acetate = 2:1 (volume ratio). An hour after the start of the reaction, an o-allylphenole spot was identified with a value $R_f = 0,55$.

Results of IR spectroscopy of allyl phenyl ether and the isomerization product, were the duration of reaction confirmed. The vibrations of the CH bond in the aromatic ring 3040,88, asymmetric stretching vibrations of the C-O-C bond 1240,09 cm^{-1} , symmetrical stretching vibrations of the C-O-C bond

1031,85 cm^{-1} , and stretching vibrations, -O-CH₂- were observed in 990.49 cm^{-1} . In the IR spectrum of isomerization products, was servented increasing the peak of stretching vibrations of the group — OH 3436.32 cm^{-1} , stretching vibrations of the CH bond in the aromatic ring 3077,36 cm^{-1} . Valence vibrations of the C-O bond were observed in the region of 1219,37-1240,15 cm^{-1} , deformation vibrations of the -OH group at 1329,17 cm^{-1} . Also, the stretching vibrations of the C-O-C bond significantly decreased, which has proved the conversion of ether into phenol.

The GC-MS results of mixture of isomerization reaction products are summarized in Table 2. The GC-MS data confirmed that the content of the o-isomer mixture was 56,39%. Other products have less concentrations which are confirmed by shift of equilibrium to 2-allylphenol and selectivity of reaction.

Conclusion

The results of the experiments showed the possibility of using small amounts of nanostructured $Fe/SiO_2 \cdot TiO_2$ catalyst in the isomerization reaction of allyl phenyl ether at a temperature of 90-95 °C. And at this, it is possible to selectively obtain with predominant yield 2-allylphenol, which is compounds that has found application in various fields of the national economy.

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