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RESEARCH ARTICLE

Development of new supported catalysts for the continuous alkylation of amines with alcohols

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Abstract

Objectives. The work set out to develop catalysts based on nickel and copper obtained by active phase chemical reduction and investigate their activity including the influence of the type of supports on the course of alkylation of amines with primary or secondary alcohols in a plug-flow reactor with a fixed catalyst bed.

Methods. The reactions were carried out in a continuous mode on a fixed bed of an appropriate catalyst in a plug flow microcatalytic apparatus at 160–240°C. NaX zeolite, magnesium oxide, and γ-Al_2O_3 were used as supports. After preparing the catalysts by impregnation from an excess solution of metal salts, the active metal phase was reduced with a sodium tetrahydridoborate aqueous solution. The composition of the resulting products was analyzed by gas–liquid chromatography, while their structure was confirmed by gas chromatography-mass spectrometry. The alkylating agents were ethanol, 2-propanol, 1-butanol, 1-pentanol, benzyl alcohol, and 1-octanol; alkylated amines were 1-butylamine, 1-hexylamine, 1-octylamine, aniline, morpholine, piperidine, and hexamethyleneimine.

Results. The alkylation of amines with alcohols catalyzed by metal (nickel and copper) nanoparticles supported on NaX zeolite, magnesium oxide MgO, and γ-Al_2O_3 in a plug-flow reactor with a fixed catalyst bed at atmospheric hydrogen pressure and 160–240°C leads to the formation of predominantly mono-*N*-alkylated products with yields up to 99%.

Conclusions. Nickel (or nickel and copper) nanoparticles supported on various supports are effective catalysts for the synthesis of secondary or tertiary amines in the plug-flow reactor.

Keywords

catalysis, nanoparticles, nickel, alkylation, alkanols

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НАУЧНАЯ СТАТЬЯ

Разработка новых нанесенных катализаторов непрерывного алкилирования аминов спиртами

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Аннотация

Цели. Расширение исследований по разработке катализаторов на основе никеля и меди, получаемых химическим восстановлением активной фазы, и по изучению влияния типа носителей на их активность в процессах алкилирования аминов первичными и вторичными спиртами в проточном реакторе с неподвижным слоем катализатора.

Методы. Процесс осуществлялся на неподвижном слое исследуемых катализаторов в проточной микрокаталитической установке при 160–240°C. В качестве носителей были использованы цеолит γ-Al_2O_3, NaX, оксид магния. Катализаторы готовились методом пропитки адсорбцией из избытка раствора солей металлов. Восстановление активной металлической фазы проводилось водным раствором тетрагидридобората натрия. Субстратами выступали первичные или вторичные амины: 1-бутиламин, 1-гексиламин, 1-октиламин, анилин, морфолин, пиперидин, гексаметиленимин. Алкилирующими агентами являлись этанол, пропанол-2, бутанол-1, пентанол-1, бензиловый спирт, октанол-1. Состав полученных продуктов анализировался газожидкостной хроматографией, их строение подтверждалось методом хромато-масс спектрометрии.

Результаты. Алкилирование спиртами аминов при катализе частицами металлов (никеля и меди), нанесенными на цеолит NaX, оксид магния MgO и γ-Al_2O_3, в проточном реакторе с неподвижным слоем катализатора при 160–240°C и атмосферном давлении водорода приводит к образованию преимущественно моно-*N*-алкилированных продуктов с выходами до 99%.

Выводы. Наночастицы никеля (или никеля и меди), нанесенные на различные носители, являются эффективными катализаторами синтеза вторичных или третичных аминов в проточном реакторе с неподвижным слоем катализатора.

Ключевые слова

катализ, наночастицы, никель, алкилирование, амины, алканолы

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INTRODUCTION

Di- and trialkylamines are of high practical importance as vulcanization accelerators and intermediate products in the production of surfactants, antioxidants, pesticides, corrosion inhibitors, absorbents, solvents, extractants, etc. The products of alkylation at the nitrogen atom are additionally used as catalysts in the synthesis of polycondensation polymers. The most applicable industrial-scale method for the synthesis of these chemicals is catalytic *N*-alkylation of ammonia or primary amines with alcohols. The advantages of this method including the wide availability of reagents and the formation of water as the only byproduct [1, 2].

Currently, the main direction of research is the development of effective catalysts for this process. For the purposes of *N*-alkylation, oxides [3–5], salts, complexes [6, 7], and nanoparticles of metals of variable valence [8–10] are used as catalysts. However, supported metal catalysts that combine the implementation of the alkylation process at moderate temperatures and ease of separation from the reaction mass are of greatest practical interest.

The authors of [11] studied aniline *N*-alkylation with benzyl alcohol in the presence of Ru/CeO_2. The reaction was carried out at 160°C using *p*-xylene as a solvent under an N_2 atmosphere for 24 h. The yield of the product was found to strongly depend on the support morphology. Ru/CeO_2–R with a rod morphology exhibits both higher activity and selectivity for the formation of *N*-benzylaniline (yield 88%) than cubic Ru/CeO_2–C (52%) and octahedral Ru/CeO_2–O (32%).

A copper catalyst on a porous *N,P*-doped carbon support obtained from wheat straw showed efficiency in the *N*-monoalkylation of aromatic amines with aromatic alcohols. The reaction was carried out in cyclohexane

as a solvent at 140°C under an argon atmosphere for 12 h. Anilines containing electron-donating groups were converted into the corresponding secondary amines in yields of 66–91% [12].

A catalyst based on palladium and carbon nitride C_3N_4 showed high activity in the synthesis of *N*-substituted aminopyridine with good regenerability indices. When carrying out the synthesis at 110°C in toluene for 12 h, the yield of the target product was 95% [13].

The authors of [14] studied the use of a catalyst based on encapsulated platinum nanoparticles and beta-zeolite in the *N*-alkylation of amines with aromatic alcohols. When carrying out aniline alkylation with benzyl alcohol at 160°C for 2.5 h under an N_2 atmosphere (1 atm), the yield of the product was 93%.

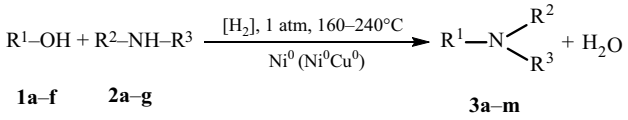
The typically long time taken for the alkylation of amines with alkanols is due to the mechanism of this complex three-stage reaction. First, the alkanol undergoes reversible dehydrogenation into an aldehyde (ketone), which then condenses with the amine; the final product is formed from the intermediate aldimine (ketimine) following its hydrogenation. As a result, a periodic method for implementing this type of process is more common. In [15], the use of nickel or copper nanoparticles deposited on γ-Al_2O_3 by a modified coprecipitation method as catalysts for the alkylation of amines with alkanols was investigated. Using this approach, it was possible to obtain target products in a continuous mode with high yields and selectivity up to 100% at 180–220°C and atmospheric hydrogen pressure.

The purpose of the present work is to accumulate the research of a group of authors on the study of the activity of catalysts based on nickel and copper nanoparticles deposited on various substrates in the continuous process of alkylation of amines with alkanols in a flow reactor with a fixed catalyst bed.

MATERIALS AND METHODS

Zeolite NaX, MgO, γ-Al_2O_3 (*EKROS*, Russia) were used as supports. The catalysts were prepared by adsorption impregnation without coprecipitants; the active metal phase was reduced with an aqueous solution of sodium tetrahydridoborate (*EKROS*, Russia). The metal content in the resulting catalysts was (wt %): Ni/MgO: 23.8; Ni/Al_2O_3: 5.0; Ni/NaX: 5.6; NiCu/Al_2O_3: Ni, 2.4, Cu, 2.3; NiCu/NaX: Ni, 5, Cu, 5.

The following primary or secondary amines served as substrates: 1-butylamine, 1-hexylamine, 1-octylamine, aniline, morpholine, piperidine, and hexamethyleneimine (*EKROS*, Russia). The alkylating agents were ethanol, 2-propanol, 1-butanol, 1-pentanol, benzyl alcohol, and 1-octanol (*EKROS*, Russia). The process was carried out using a flow-through microcatalytic unit (*Meta-Khrom*, Russia) in continuous mode on a fixed catalyst bed at 160–240°C. A small amount of hydrogen was supplied using a GV-7 hydrogen generator (*Meta-Khrom*, Russia) as a diluent and for exhaustive hydrogenation of intermediate imines or enamines (Figure).



R^1 = Et (**1a**), *i*-Pr (**1b**), Bu (**1c**), C_5H_{11} (**1d**), $C_6H_5CH_2$ (**1e**), C_8H_{17} (**1f**).
R^2 = H; R^3 = Bu (**2a**), C_6H_{13} (**2b**), C_8H_{17} (**2c**), C_6H_5 (**2d**);
R^2–R^3 = $(CH_2CH_2)_2O$ (**2e**), $(CH_2)_5$ (**2f**), $(CH_2)_6$ (**2g**).
R^1 = *i*-Pr, R^2 = H, R^3 = C_6H_{13} (**3a**), C_8H_{17} (**3b**);
R^1 = Bu, R^2–R^3 = $(CH_2)_5$ (**3c**); R^2 = H, R^3 = C_6H_5 (**3g**);
R^1 = C_5H_{11}, R^2–R^3 = $(CH_2)_5$ (**3d**); $(CH_2CH_2)_2O$ (**3e**);
R^2 = H, R^3 = C_6H_5 (**3h**); R^1 = Et, R^2 = H, R^3 = C_6H_5 (**3f**);
R^1 = $C_6H_5CH_2$, R^2 = H, R^3 = C_6H_{13} (**3i**); R^3 = C_8H_{17} (**3j**);
R^1 = C_8H_{17}, R^2 = H, R^3 = C_6H_{13} (**3k**); R^2–R^3 = $(CH_2)_5$ (**3l**);
R^2–R^3 = $(CH_2)_6$ (**3m**)

Fig. Reaction scheme

The composition of the catalyzate was established by gas–liquid chromatography. The structure of the target products **3a**–**m** was confirmed by chromatography-mass spectrometry. Chromatographic mass spectrometry was performed on a Saturn 2100 T/GC3900 instrument (*Varian*, USA) using electron impact (EI) ionization with an ionization energy of 70 eV. Chromatographic analysis was performed on a Crystallux 4000M chromatograph (*Meta-Khrom*, Russia) with an HP-5 column (*Agilent Technologies*, USA) at a column temperature of 100°C and evaporator temperature of 250°C. Scanning electron microscopy was performed using a FEI Versa 3D DualBeam instrument (*FEI*, USA). Elemental analysis was carried out by energy-dispersive X-ray spectroscopy (EDS) using FEI Versa 3D DualBeam (*FEI*, USA).

RESULTS AND DISCUSSION

At a temperature range of 180–220°C and atmospheric hydrogen pressure with a liquid reagent load of 1.8–3.6 L/(kg_{cat}·h), the conversion of the initial amines **2a**–**g** reached 99%. Nickel nanoparticles supported on MgO or Al_2O_3 were shown to selectively catalyze the monoalkylation of primary amines. In this case, the use of reagent ratios close to equimolar is accompanied by a side process of disproportionation of the initial primary amines, which was described earlier for the studied type of catalysts [16]. As the alkanol

excess increases twofold, the selectivity for the target products increases to 98%. When using zeolite NaX as a substrate, the selectivity of the monoalkylation reaction of primary amines decreases, while forming up to 40% of tertiary amines [17].

Thus, the chemically reduced nickel phase on different supports demonstrated strong catalytic activity with high selectivity for the formation of monoalkylated products observed on MgO and γ-Al_2O_3. In addition to the excess of the initial alkanols, no traces of the corresponding carbonyl compounds were found in the catalyzate. This indicates that alkylation is limited by the alkanol dehydrogenation stage. Since copper is a known catalyst for alcohol dehydrogenation, it becomes interesting to study its promoting effect on the alkylation of amines with alkanols.

Further studies showed that the catalyst obtained by reducing nickel and copper ions coprecipitated in a 1 : 1 ratio on NaX zeolite (Ni^0Cu^0/NaX) or on pressed magnesium oxide (Ni^0Cu^0/NaX) was more effective as compared to the nickel ones described above. In particular, the target *N*-alkylanilines were obtained in 66–85% yields with a process selectivity of 83–89% by the alkylation of aniline with ethanol, 1-butanol or 1-pentanol at a temperature of 240°C on the Cu^0Ni^0/NaX catalyst. In addition to *N*-ethylaniline (**3f**) (71.1%), *N,N*-diethylaniline (13.5%) was formed. For alkanols with a higher molecular weight, an increase in selectivity was observed. For example, when obtaining *N*-1-butylaniline (**3g**), the conversion of aniline (**2g**) and the reaction selectivity took on maximum values (95.1% and 89.5%, respectively) [18].

Alkylation of morpholine (**2e**) with 1-pentanol (**1d**) on the Ni^0Cu^0/MgO catalyst occurs in the temperature range of 100–200°C at an increased morpholine conversion from 8 to 100% and 1-pentylmorpholine (**3e**) yield ranging from 4 to 92.5%. However, a similar nickel-free catalyst obtained by reducing copper chloride on magnesium oxide (Cu^0/MgO) showed low activity (the morpholine conversion at 200–220°C was 10–15%, while the yield of 1-pentylmorpholine was 4–14%). The conversion of morpholine during its alkylation with 1-pentanol on Ni^0/MgO or Ni^0/Al_2O_3 catalysts at 180°C did not exceed 50%, while the product yield was 36% (on Ni^0/Al_2O_3) and 18% (on Ni^0/MgO). In the latter case, 15% of the corresponding enamine is also formed. Thus, the activity of metals in the catalysis of this reaction is in the series Cu < Ni < Cu–Ni.

EXPERIMENTAL

The catalysts were prepared according to the methods described in [16–18].

Conducting reactions

Isopropyl-1-hexylamine (3a). Hydrogen was fed to the Cu^0Ni^0/Al_2O_3 catalyst at a flow rate of 1 L/h and a mixture of 2-propanol (**1b**) and 1-hexylamine (**2b**) with a molar ratio of **1b** : **2b** = 10 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 220°C. Conversion of 1-hexylamine was 100%. Selectivity was 98%. The yield of isopropyl-1-hexylamine was 98%. Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 144.0 (17) [M^{+1}], 143.1 (23) [M], 72.0 (100), 44.2 (35), 30.3 (60).

Isopropyl-1-octylamine (3b). Hydrogen at a flow rate of 1 L/h and a mixture of 2-propanol (**1b**) and 1-octylamine (**2c**) with a molar ratio of **1b** : **2c** = 10 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 180°C were fed to the Ni^0/Al_2O_3 catalyst. Conversion of 1-octylamine was 99%. Selectivity was 97%. The yield of isopropyl-1-octylamine was 96%. Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 172.2 (5) [M^{+1}], 171.1 (16) [M], 113.2 (100), 55.2 (6), 44.1 (26).

1-Butylpiperidine (3c). a) Hydrogen at a flow rate of 1 L/h and a mixture of 1-butanol (**1c**) and piperidine (**2f**) with a molar ratio of **1c** : **2f** = 2.5 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 200°C were fed to the Cu^0Ni^0/Al_2O_3 catalyst. Piperidine conversion was 99%. Selectivity was 98%. The yield of 1-butylpiperidine was 97%. Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 141.9 (6) [M^{+1}], 140.7 (2) [M], 139.9 (5), 98.9 (6), 98 (100), 70 (10), 42.1 (7).

b) Hydrogen at a flow rate of 1 L/h and a mixture of 1-butanol (**1c**) and piperidine (**2f**) with a molar ratio of **1c** : **2f** = 2.5 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 200°C were fed to the Ni^0/Al_2O_3 catalyst. Piperidine conversion was 99%. Selectivity was 92.4%. The yield of 1-butylpiperidine was 91.5%.

c) Hydrogen at a flow rate of 3 L/h and a mixture of 1-butanol (**1c**) and piperidine (**2f**) with a molar ratio of **1c** : **2f** = 4 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 240°C were fed to the Ni^0/Al_2O_3 catalyst. Piperidine conversion was 45.5%. Selectivity was 100%. The yield of 1-butylpiperidine was 45.5%.

1-Pentylpiperidine (3d). Hydrogen at a flow rate of 3 L/h and a mixture of 1-pentanol (**1d**) and piperidine (**2f**) with a molar ratio of **1d** : **2f** = 3 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 200°C were fed to the Cu^0Ni^0/Al_2O_3 catalyst. Piperidine conversion was 98.5%. Selectivity was 100%. The yield of 1-pentylpiperidine was 98.5%. Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 159.1 (2) [M^{+2}], 158.0 (32) [M^{+1}], 156.1 (6) [M], 126.0 (5), 100.0 (100), 98.3 (5), 70.1 (12), 56.1 (2).

1-Pentylmorpholine (3e). a) Hydrogen at a flow rate of 1 L/h and a mixture of 1-pentanol (**1d**) and morpholine (**2f**) with a molar ratio of **1d** : **2f** = 1 : 1 with a flow rate of 3.6 L/(kg_{cat}·h) at 240°C were fed to the Cu^0Ni^0/NaX catalyst.

Morpholine conversion was 85%. Selectivity was 97%. The yield of 1-pentylmorpholine was 82.5%. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 158.1 (28) [M^{+1}], 100.1 (100), 99.2 (7), 70.1 (12).

b) Hydrogen at a flow rate of 1 L/h and a mixture of 1-pentanol (**1d**) and morpholine (**2f**) with a molar ratio of **1d** : **2f** = 3 : 1 with a flow rate of 1.8 L/(kg_{cat}·h) at 160°C were fed to the Cu^0Ni^0/MgO (1 : 1) catalyst. Morpholine conversion was 99.5%. Selectivity was 93%. The yield of 1-pentylmorpholine was 92.5%.

c) Hydrogen at a flow rate of 1 L/h and a mixture of 1-pentanol (**1d**) and morpholine (**2f**) with a molar ratio of **1d** : **2f** = 5 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 180°C were fed to the Ni^0/Al_2O_3 catalyst. Morpholine conversion was 50.3%. Selectivity was 98%. The yield of 1-pentylmorpholine was 49.3%.

d) Hydrogen at a flow rate of 1 L/h and a mixture of 1-pentanol (**1d**) and morpholine (**2f**) with a molar ratio of **1d** : **2f** = 5 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 220 °C were fed to the Cu^0/MgO catalyst. Morpholine conversion was 25%. Selectivity was 98%. The yield of 1-pentylmorpholine was 24.5%.

The compounds *N*-ethylaniline (**3f**), *N*-1-butylaniline (**3g**), *N*-1-pentylaniline (**3h**) were prepared in a manner similar to that described in [18].

***N*-Benzyl-1-hexylamine (3i).** Hydrogen at a flow rate of 0.3 L/h and a mixture of benzyl alcohol (**1e**) and 1-hexylamine (**2b**) with a molar ratio of **1e** : **2b** = 1 : 1 at a flow rate of 3.6 L/(kg_{cat}·h) at 240°C were fed to the Ni^0/NaX catalyst. The conversion of 1-hexylamine was 98%. Selectivity was 70%. The yield of *N*-benzyl-1-hexylamine was 68.6%, mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 193.0 (4) [M^{+2}], 192.0 (32) [M^{+1}], 190.1 (4), 119.8 (65), 106.0 (15), 92.0 (8), 91.1 (100), 65.0 (9), 41.0 (5). The yield of di-1-hexylamine (byproduct) was 24.2%, mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 187.0 (12) [M^{+2}], 186.1 (100) [M^{+1}], 184.3 (2), 114.2 (34), 44.0 (84), 41.0 (7). The yield of *N*-hexyl-1-benzylimine (byproduct) was 5.3%, mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 191.0 (5) [M^{+2}], 190.1 (31) [M^{+1}], 189.0 (2) [M^{+}], 174.0 (7), 160.0 (100), 146.1 (10), 131.9 (34), 118.0 (54), 104.0 (23), 91.1 (78), 77.1 (11), 65.0 (11), 41.0 (13.5).

***N*-Benzyl-1-octylamine (3j)**. Hydrogen at a flow rate of 0.3 L/h and a mixture of benzyl alcohol (**1e**) and 1-octylamine (**2c**) with a molar ratio of **1e** : **2c** = 1.1 : 1 were fed to the Ni^0/NaX catalyst at a flow rate of 1.8 L/(kg_{cat}·h) at 220°C. The conversion of 1-octylamine was 98.5%. Selectivity was 53.3%. *N*-Benzyl-1-octylamine, yield 52.5%, mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 220.1 (51) [M^{+2}], 218.2 (5) [M], 128.0 (8), 121.0 (7), 119.9 (80), 106.0 (13.6), 92.0 (7.4), 91.1 (100), 65.0 (8), 41.0 (7). Benzyl-1-octylimine (byproduct), yield 6.3%, mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 218.1 (97) [M^{+2}], 216.2 (7) [M], 174.1 (19), 160.0 (100), 132.1 (26), 118.2 (41), 91.1 (45), 77.2 (5), 65 (7), 51.0 (6), 41.0 (14). Di-1-octylamine (byproduct), yield 40.2%, mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 243.3 (16) [M^{+2}], 242.3 (100) [M^{+1}], 142.2 (9.4), 44.0 (44).

***N*-1-Hexyl-1-octylamine (3k)**. Hydrogen at a flow rate of 3 L/h and a mixture of 1-octanol (**1f**) and 1-hexylamine (**2b**) with a molar ratio of **1f** : **2b** = 2 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 220°C were fed to the Ni^0/MgO catalyst. The conversion of 1-hexylamine was 99%. Selectivity was 98%. The yield of *N*-1-hexyl-1-octylamine was 97%. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 215.1 (14.5) [M^{+2}], 214.2 (83) [M^{+1}], 212.3 (4), 142.0 (21), 114.0 (31), 44.0 (100).

1-Octylpiperidine (3l). Hydrogen at a flow rate of 4 L/h and a mixture of 1-octanol (**1f**) and piperidine (**2f**) with a molar ratio of **1f** : **2f** = 3 : 1 at a flow rate of 1.8 L/(kg_{cat}·h) at 180°C were fed to the Cu^0Ni^0/NaX catalyst. Piperidine conversion was 93.7%. Selectivity was 100%. The yield of 1-oct-1-yl-piperidine was 93.7%. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 199.1 (4) [M^{+2}], 198.2 (25) [M^{+1}], 196.2 (8), 98.2 (100), 70.2 (8).

1-Octyl-1-azacycloheptane (3m). Hydrogen at a flow rate of 2 L/h and a mixture of 1-octanol (**1f**) and hexamethyleneimine (**2g**) with a molar ratio of **1f** : **2g** = 3 : 1 with a flow rate of 1.8 L/(kg_{cat}·h) at 240°C were fed to the Ni^0/Al_2O_3 catalyst. Hexamethyleneimine conversion was 97%. Selectivity was 100%. The yield of 1-octyl-1-azacycloheptane was 97%. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 211.0 (10) [M], 99 (7), 98.1 (100).

CONCLUSIONS

The reported studies confirm that heterogeneous catalysts containing nickel (or nickel and copper) nanoparticles obtained by chemical reduction and deposited on various carriers (zeolite NaX, magnesium oxide MgO, γ-Al_2O_3) in amine alkylation reactions with alcohols in the temperature range of 160–240°C and at atmospheric pressure exhibit high catalytic activity to obtain target products with yields of up to 99% and selectivity of 53–100% in a continuous process mode.

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Authors' contributions

V.M. Mokhov—developing the experiment, conducting experimental studies, writing the text of the article.

D.N. Nebykov—developing the research concept, analyzing the results, writing the text of the article.

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