SPECIFIC
TECHNOLOGICAL PROCESSES

Continuous Production of Dialkylamines by Selective Hydrogenation of Nitriles on a Nickel-Zeolite Catalyst

Yu. V. Popov*, V. M. Mokhov, S. E. Latyshova, A. O. Panov, and M. Yu. Pletneva

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia
*e-mail: tons@vstu.ru

Abstract—Hydrogenation of aliphatic nitriles in the presence of nickel supported by NaX zeolite was studied. The data obtained were used to develop a continuous method for obtaining dialkylamines with the yield of the target product of up to 98%.

At the annual world's production of more than 1.9 million tons (according to the data for 2013), aliphatic amines C_1–C_6 are used in many fields of industry, agriculture, and medicine [1, 2]. In turn, aliphatic diamines are important half-products of organic synthesis. For example, di-*n*-propylamine and di-iso-butylamine are for the most part used in syntheses of herbicides. Di-*n*-butylamine is used for synthesis of sulfonamide vulcanization accelerators [1].

Using the hydrogenation of nitriles in order to obtain secondary amines is a possible alternative to the existing industrial methods for their synthesis via alkylation of ammonia by alcohols.

It is known from the literature that the hydrogenation of nitriles yields a mixture of primary, secondary, and tertiary amines [3]. A promising way is to use catalysts providing a selective synthesis of products. For example, the authors of [4] described the selective hydrogenation of aliphatic nitriles to give secondary amines in 94–100% yield in the presence of Rh/C under atmospheric pressure at a temperature of 25–60°C in the course of 6–24 h in cyclohexane. The hydrogenation of aromatic nitriles and cyclohexanecarbonitrile under similar conditions selectively produced in 82–100% yield secondary amines in the presence of both Pd/C and Rh/C [4].

The gas-phase hydrogenation has been studied in most detail for acetonitrile. For example, the authors of [5] used as a catalyst nickel on supports containing tin phosphate and aluminum oxide or a mixed aluminum-gallium oxide. The conversion under atmospheric pressure at a temperature of 125°C reached values of 10–100%, with the selectivity with respect to diethylamine being 33–44%.

In [6], the role of a catalyst was played by nickel supported by mesoporous silicon oxide modified with zirconium. The process was performed under atmospheric pressure at 135°C, with the conversion reaching a value of 11–31% and the selectivity with respect to diethylamine being 25–39%.

Palladium deposited on various supports (ZrO_2, CeO_2, MgO, SiO_2, Al_2O_3, ZnO, Ga_2O_3, and In_2O_3) was used in the reaction of acetonitrile hydrogenation at 170°C under atmospheric pressure. The conversion of the nitrile reached values of 30–99%, with the selectivity with respect to diethylamine being 25–48%.

Previously, we have studied [8] continuous processes for hydrogenation of nitriles of varied structure on a catalyst having the form of nanostructured agglomerates of nickel particles, supported by a cracking catalyst Ceokar-2. With the hydrogenation performed at 120–260°C under atmospheric pressure , a mixture of products was obtained, which included di- and trialkylamines, with yields of secondary amines of 3 to 96%, depending on the nitrile structure and temperature. The catalyst preserved its activity during 15 h of continuous operation.

The methods described above have a number of disadvantages, such as application of expensive and

hard-to-get materials, or a low formation selectivity of the target product.

The goal of our study was to develop a selective method for continuous hydrogenation of nitriles into secondary amines with gaseous hydrogen on a readily available catalyst under mild conditions.

EXPERIMENTAL

We used the following reagents: propionitrile (99%), *n*-butyronitrile (99%), nickel chloride hexahydrate (99.3%), and sodium tetrahydroborate (97%) from Alfa Aesar; iso-butyronitrile (99%) and n-valeronitrile (88%) from Acros Organics; NaX zeolite [TU (Technical Specification) 2163-003-21742510–2004] from ReaKhim.

A chromato-mass-spectral analysis was made on a Saturn 2100 T/GC3900 instrument (electron impact EI, 70 eV).

A GLC analysis of the reaction mass was made on a Kristallyuks-4000M chromatograph at t_{heat} = 100–210°C, t_{evap} = 250°C, Agilent HP-5 polar column, l_{col} = 50 m, d_{col} = 0.32 mm, carrier-gas nitrogen, photoinization detector (PID), t_{PID} = 250°C.

An elemental analysis of the catalyst was made by energy-dispersive X-ray spectroscopy (EDS) with a FEI Versa 3D DualBeam instrument.

Catalyst preparation. A 2-g portion of the NaX zeolite (1–1.5 mm fraction) was impregnated with an aqueous solution of 0.5 g nickel chloride $NiCl_2 \cdot 6H_2O$ in 4 mL of water in the course of 24 h. The impregnated support was filtered off and washed with distilled water. Nickel ions were reduced with three 0.1-g portions of $NaBH_4$ at a temperature of 22–25°C, with 2–3 mL per portion.

Hydrogenation. The reaction was performed in a flow-through displacement reactor under atmospheric pressure in the temperature range 120–240°C. The reduced catalyst (2 g) was charged into the reactor in the humid form between glass package layers, and water was removed in a flow of hydrogen at 120°C immediately before the reaction. The laboratory reactor has the form of a tube made of 12Kh18N10T steel with inner diameter of 9 mm and heating-zone height of 50 mm, placed in an electric furnace. The temperature within the reactor was measured with a thermocouple. The hydrogen flow rate was controlled with a GV-7 hydrogen generator.

Hydrogenation of *iso*-butyronitrile (1a). The conditional residence time of hydrogen was 40 s kg_{cat} mol^{-1}, and that of nitrile **1a**, 119 s kg_{cat} mol^{-1}. The reaction was performed at 220°C. The conversion of nitrile **1a** was 100%. The selectivity with respect to di-iso-butylamine **4a** was 98%, and its yield, 98%. Mass spectrum (EI, 70 eV), m/e ((I_{rel}, %): 130.0 (16) [$M + 1$], 128.7 (2) [M], 86.0 (100), 57.0 (30), 41.0 (30), 44.0 (19), 42.1 (10). The selectivity with respect to *N-iso*-butylidene-*iso*-butylamine **3a** was 2%, and its yield, 2%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 128.0 (34) [$M + 1$], 126.8 (6) [M], 84.0 (100), 41.0 (57), 56.9 (51), 56.0 (40), 42.0 (26), 70.0 (10).

Hydrogenation of propionitrile (1b). The conditional residence time of hydrogen was 40 s kg_{cat} mol^{-1}, and that of nitrile 1b, 278 s kg_{cat} mol^{-1}. The temperature was 220°C. The conversion of nitrile **1b** was 100%. The selectivity with respect to di-iso-butylamine **4b** was 89%, and its yield, 89%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 102.0 (76) [$M + 1$], 100.8 (7) [M], 72.0 (100), 44.0 (87), 41.1 (32), 43.0 (27), 42.0 (17). The selectivity with respect to tri-*n*-propylamine **6b** was 8.5%, and its yield, 8.5%, Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 143.9 (10) [$M + 1$], 143.1 (1) [M], 113.9 (100), 85.9 (60), 58.0 (12), 43.9 (9), 115.0 (8), 142.0 (5). The selectivity with respect to *N*-propylidenepropylamine **3b** was 2.5%, and its yield, 2.5%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 99.9 (21) [$M + 1$], 98.9 (6) [M], 69.9 (100), 42.0 (59), 41.0 (50), 43.0 (45).

Hydrogenation of *n*-butyronitrile (1c). The conditional residence time of hydrogen was 40 s kg_{cat} mol^{-1}, and that of nitrile **1c**, 174 s kg_{cat} mol^{-1}. The reaction was performed at 200°C. The conversion of nitrile **1c** was 100%. The selectivity with respect to di-*n*-butylamine **4c** was 85%, and its yield, 85%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 130.0 (26) [$M + 1$], 128.7 (2) [M], 44.1 (100), 85.9 (39), 41.1 (31), 42.0 (17), 57.0 (62), 43.0 (5). The selectivity with respect to tri-*n*-butylamine **6c** was 13%, and its yield, 13%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 186.0 (16) [$M + 1$], 142.0 (100), 99.9 (90), 58.0 (60), 143.0 (10), 141.1 (8). The selectivity with respect to butyl-1-idene-di-*n*-butylamine **3c** was 2%, and its yield, 2%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 184.2 (2) [$M + 1$], 44.0 (100), 85.9 (49), 41.1 (12), 57.0 (55), 156.1 (4).
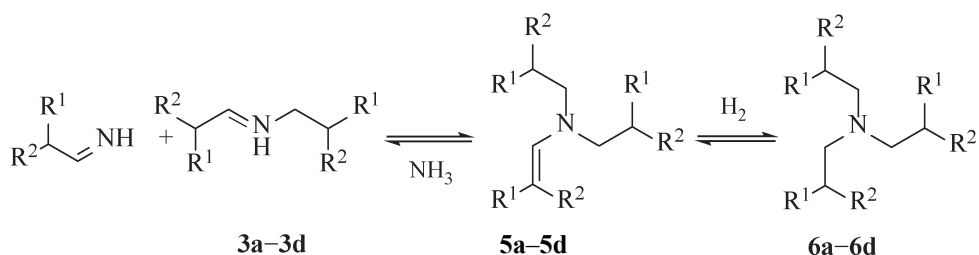
Hydrogenation of *n*-valeronitrile (1d). The conditional residence time of hydrogen was 54 s kg_{cat} mol^{-1}, and that of nitrile **1d**, 418 s kg_{cat} mol^{-1}. The reaction was

Scheme 1.
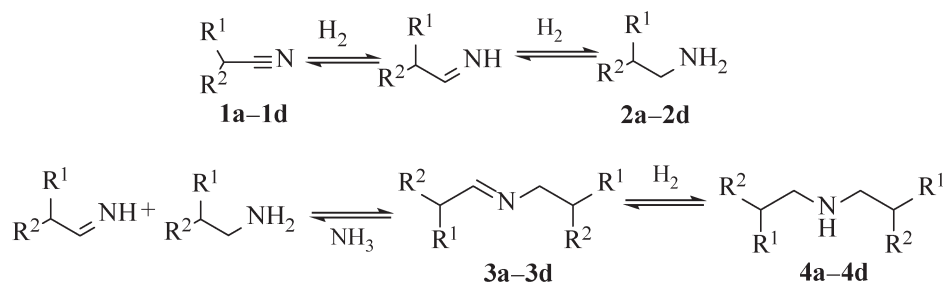
R^1 = Me (**1a,1b−4a,4b**), Et(**1c−4c**), Pr(**1d−4d**); R^2 = Me(**1a−4a**), H(**1b,1c,1d−4b,4c,4d**).

Scheme 2.

R^1 = Me (**3a,3b−6a,6b**), Et (**3c−6c**), Pr (**3d−6d**); R^2 = Me (**3a−6a**), H (**3b,c,d−6b,c,d**).

performed at 200°C. The conversion of nitrile **1d** was 100%. The selectivity with respect to di-n-pentylamine **4d** was 63%, and its yield, 63%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 158.0 (36) [$M + 1$], 156.8 (2) [M], 44.0 (100), 100.0 (47), 43.0 (12), 41.0 (9). The selectivity with respect to di-n-pentylamine **6d** was 11%, and its yield, 11%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 228.2 (14) [$M + 1$], 170.0 (100), 114.0 (55), 58.0 (40), 171.0 (12). The selectivity with respect to N-pentylidenepentylamine **3d** was 1%, and its yield, 1%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 156.0 (100) [M+1], 98.1 (94), 41.0 (29), 42.0 (25), 56.0 (24). The selectivity with respect to n-pentylamine 2d was 25%, and its yield, 24%. Mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 87.8 (100) [M+1], 86.9 (19), 86.0 (6), 83.9 (2), 82.8 (1).

RESULTS AND DISCUSSION

The catalyst was produced by impregnation of a support with an aqueous solution of nickel chloride, with the subsequent reduction with $NaBH_4$ in water, as this was done in [8]. A zeolite of NaX brand (TU 2163-003-21742510–2004) was chosen as the support. As a result, we obtained a catalyst whose surface contains, according to the results of energy-dispersive X-ray spectroscopy, 5.6% Ni, 19.2% Si, 13.8% Al, 10.7% Na, and 50.66% O.

We used the catalyst to examine the hydrogenation of iso-butyronitrile **1a**, propionitrile **1b**, n-butyronitrile **1c**, and n-valeronitrile **1d** in the temperature range 120–240°C under atmospheric pressure. The composition and structure of the products were confirmed by gas-liquid chromatography and chromato-mass-spectrometry. It was found the catalyst retained its activity after 15 h of continuous operation.

The main reaction products at 180–240°C were symmetric dialkylamines **4a–4d**, formed by Scheme 1. The corresponding tertiary amines were formed as by-products by Scheme 2.

In all cases, insignificant amounts (1–5%) of unsaturated products (imines **3a–3d** and enamines **5a–5d**) were formed.

We examined for the example of the reaction of hydrogenation of nitrile **1a** the influence exerted by the process temperature and excess of hydrogen on the conversion of the nitrile and selectivity with respect to formation of a secondary amine (Fig. 1).
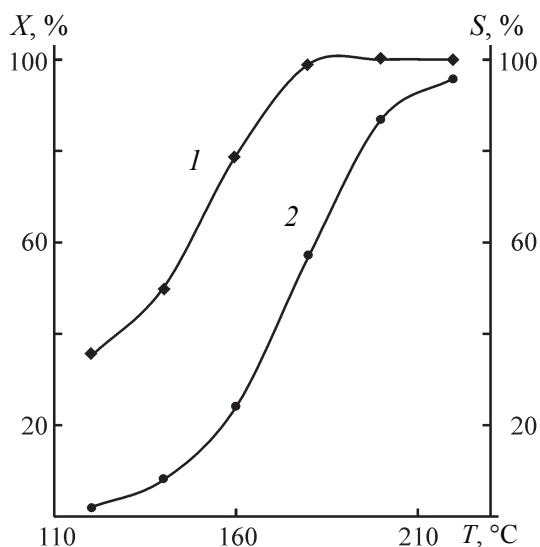
Fig. 1. (*1*) Conversion *X* of *iso*-butyronitrile **1a** and (*2*) formation selectivity *S* of di-*iso*-butylamine **4a** vs. temperature *T*.

Fig. 2. Formation selectivity *S* of di-isobutylamine **4a** vs. molar excess of hydrogen H_2 at 180°C.

At a temperature of 120°C, the conversion of nitrile **1a** was 35%, with *N-iso*-butylidene-*iso*-butylamine **3a** being the main reaction product and iso-butylamine **2a** formed as a by-product with selectivity of 16%. When the temperature was raised, the yield of di-*iso*-butylamine **4a** increased and that of imine **3a** and primary amine **2a** decreased with increasing conversion of nitrile. For example, the catalyzate contained at 180°C 57% dialkylamine **4a**, 23% imine **3a**, and 20% amine **2a**. The full conversion of nitrile **1a** was reached at 180°C, and the maximum selectivity with respect to secondary amine **4a** (98%), at 220°C. The high selectivity with respect to dialkylamine can be attributed to the steric hindrance to the formation of tri-*iso*-butylamine **6a**.

A study of the influence exerted by the molar excess of hydrogen at 180°C (Fig. 2) demonstrated that, as the iso-butyronitrile : hydrogen ratio is raised from 1 : 3 to 1 : 5, the selectivity with respect to secondary amine **4a** grows from 57 to 88% at a 100% conversion of nitrile **1a**. Raising the excess of hydrogen further has no effect on the course of the process. At temperatures of 200°C and more, this influence is not so significant: at ratios of 1 : 3 and 1 : 5, a 87% selectivity with respect to secondary amine **4a** is observed.

At a temperature of 220°C, we examined the influence exerted by the conditional residence time on the composition of products formed in hydrogenation of nitrile **1a**. It was found that the values of conversion (100%) and selectivity (97%) are preserved at a conditional residence time in the range 72–358 s kg_{cat} mol^{-1} at a
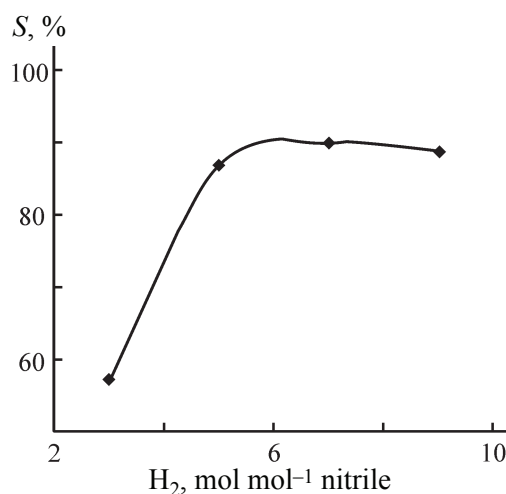
nitrile : hydrogen molar ratio of 1 : 3. In this case, the maximum specific output capacity for di-*iso*-butylamine (0.007 mol s^{-1} kg_{cat}) is reached at a specific molar expenditure of the starting nitrile of 0.014 mol s kg_{cat}.

Similar dependences were also observed in hydrogenation of nitriles with normal structure C_3–C_5 **1b**–**1d**. In the case of hydrogenation of nitrile 1b, the 100% conversion was reached at 220°C, with di-*n*-propylamine **4b** being the main product with selectivity of 89%, In the case of hydrogenation of nitrile **1c**, the 100% conversion was reached already at 200°C, with the formation selectivity of di-*n*-butylamine **4c** being 85%. In this case, the yield and selectivity with respect to secondary amine **4c** were preserved at a conditional residence time of nitrile **1c** in the range 174–347 s kg_{cat} mol^{-1} and conditional residence time of hydrogen of 32–81 s kg_{cat} mol^{-1}, respectively. A lower formation selectivity of di-*n*-pentylamine **4d** was observed for nitrile **1d**. At 200°C and 99% conversion of nitrile, dialkylamine **4d** was obtained with selectivity of 63%. As by-products, we obtained tri-*n*-pentylamine **6d** and *n*-pentylamine **2d** with selectivities of 11 and 24%, respectively. In this case, raising the temperature further to 220–240°C does not change the composition of the catalyzate.

CONCLUSIONS

A continuous process was developed for selective catalytic hydrogenation of aliphatic nitriles C_3–C_5 into the corresponding secondary amines in the presence of a

nickel-zeolite catalyst, with a selectivity of up to 98% at a 100% conversion of nitriles. The influence exerted by the excess of hydrogen and temperature on the conversion and selectivity of the process was examined. It was found that the optimal temperature range is 200–220°C, and the optimal nitrile : H_2 ratios, 1 : 3–1 : 8.

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