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Dehydrogenation of *N*-ethyldodecahydrocarbazole over Pt/C catalyst in the hydrogen storage aspect

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1. Materials and methods

1.1 Procedure of hydrogenation and dehydrogenation.

A sample of *N*-ethyldodecahydrocarbazole (5.9 wt.% H_2) was obtained by hydrogenation of commercial *N*-ethylcarbazole (99.5%; Air Products, USA). Catalyst Pd/SiO_2 based on palladium (Pd) as an active component in the amount of 4 wt.% dispersed on the surface of silica carrier was used for hydrogenation of substrates. The catalyst was prepared by impregnation of the carrier with an aqueous solution of H_2PdCl_4 followed by reduction at 320 °C in a hydrogen current of 30 ml min^{-1} for 2 hours.

The dehydrogenation reaction was carried out in a flow-type catalytic unit in the presence of prepared catalyst 3 wt.% Pt/C (sibunite, IPPU SB RAS, Omsk). Platinum was dispersed on the surface of the carbon carrier by impregnation of the carrier with aqueous solution of [H_2PtCl_6] (ωPt = 36.3%) according to the method [A. N. Kalenchuk, V. I. Bogdan, S. F. Dunaev and L. M. Kustov, *Int. J. Hydrogen Energy*, 2018, **43**, 6191; https://doi.org/10.1016/j.ijhydene.2018.01.121]. The catalyst was activated at 320°C in a hydrogen current of 30 ml min^{-1} for 2 h immediately before the reaction. Dehydrogenation of the *N*-ethyldodecahydrocarbazole sample was carried out at normal pressure in the temperature range T = 160-220 °C at volumetric rates of substrate feed V_L = 1-2.5 h^{-1}. The amount of hydrogen in liters released within an hour was taken as a criterion of substrate activity. The schematic diagram of the unit and the methodology of the experiment are given in [A. N. Kalenchuk and V. I. Bogdan, *Catal. Ind.*, 2023, **15**, 165; https://doi.org/10.1134/S2070050423020083]. The substrate cooling system together with the use of filters and traps, including membrane traps, allowed to obtain chemically pure hydrogen at the outlet without impurities of by-product gases.

1.2 Analysis of reactions products.

The reaction products were analyzed on a Cristalux-4000M chromatograph using a ZB-5 capillary column (ZEBRON, USA) on a flame ionization detector (FID). The analysis was performed in programmed mode 70-220 °C at a heating rate of 6 K min^{-1}. Separate samples for detailed identification of semi-hydrogenated and possible by-products were analyzed on a FOCUS DSQ II chromatomass spectrometer with a TR-5ms capillary column.

Conversion (X) was calculated using the formula: $X = (c_o - c)/c_o \times 100\%$, where c_o and c are the initial and final concentrations of the substrate to be converted. Selectivity (S) was calculated using the formula: $S(i) = \sum c(i) / \sum c(k) \times 100\%$, where $\sum c(i)$ and $\sum c(k)$ are the sum of the concentrations of the product group and all reaction products, respectively.

2. Supplementary information

Figure S1

Figure S1 shows the chromatogram of the sample of *N*-ethyldodecahydrocarbazole **2** used for dehydrogenation. The chromatogram contains several peaks with a retention time (t_{ret}) in the range of 11 to 18 min. Five of them were identified as stereoisomers of compound **2** by chromato-mass spectrometry, which is in agreement with literature data [F. Sotoodeh, B. J. M. Huber and K. J. Smith, *Int. J. Hydrogen Energy*, 2012, **37**, 2715; https://doi.org/10.1016/j.ijhydene.2011.03.055]. The overall selectivity for these five isomers of compound **2** was about 77%. Unfortunately, the remaining peaks could not be identified due to the absence in the database, which, however, did not serve as an obstacle to fulfill the purpose of the study.

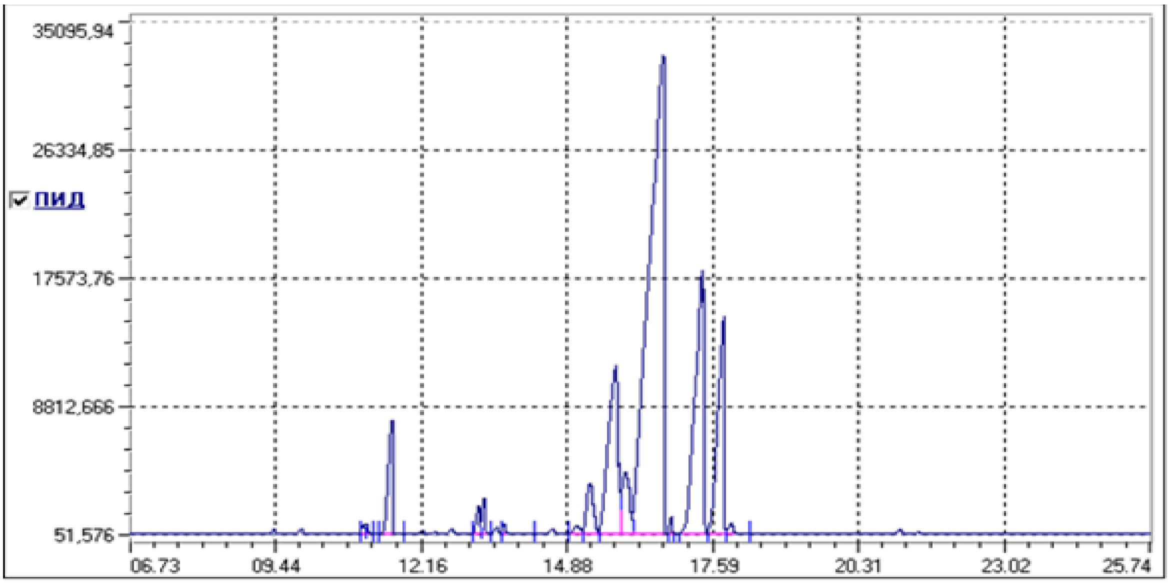

Figure S1 Chromatogram of the tested sample of *N*-ethyldodecahydrocarbazole.

Table S1 Dehydrogenation of *N*-ethyldodecahydrocarbazole ($C_{14}H_{25}N$) into *N*-ethylcarbazole **1** ($C_{14}H_{13}N$) on 3 wt.% Pt/C catalyst (T=210 °C, V_L =1 h^{-1}, P = 1 atm)

Entry	Time,	Conversion		Selectivity, *S*, %		
	t hour	*X*, %	$C_{14}H_{13}N$	$C_{14}H_{21}N$	$C_{14}H_{19}N$	$C_{14}H_{17}N$
1	2	94.0	52	23	0.3	6
2	4	94.6	53	21	0.3	6
3	6	94.2	55	15	3	4