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A Catalyst for the Selective Dehydrogenation of 4,5,6,7-Tetrahydroindole into Indole

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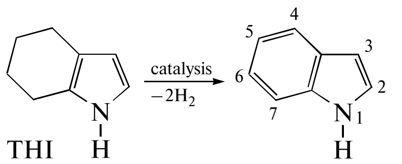
Indole is widely used for preparation of perfume formulations, pharmaceuticals [1, 2], catalysts for olefin polymerization [3], epoxy resins [4], and materials for optoelectronics [5, 6].

Aromatization of 4,5,6,7-tetrahydroindole (THI) is an expedient method for indole preparation.



Initial THI is obtained by the Trofimov reaction [7] from commercially available cyclohexanone oxime (an intermediate of caprolactam synthesis) and acetylene in a yield up to 97% [8].

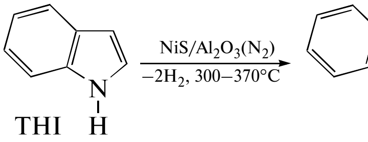
A catalytic system for dehydrogenation of 1-benzyl-3-phenyl-4,5,6,7-tetrahydroindole into 1-benzyl-3-phenylindole comprising 10% of palladium on activated carbon is known [9]. However, this catalytic system provides the dehydrogenation of substituted THI and therefore could not be directly applied to THI. Moreover, the reaction is carried out at 140°C (boiling xylene) for 2 days (indole yield is 76%). The low process rate and high palladium content in the catalytic system are unacceptable for technology application.

Indole has been obtained by dehydrogenation of a mixture of 1-vinyl-4,5,6,7-tetrahydroindole (VTHI) and THI on catalytic systems containing palladium or a mixture of chromium–rare earth oxides at 200–525°C [10]. The reaction led to a complex mixture of products containing VTHI, THI, 1-ethyl-4,5,6,7-tetrahydroindole, 1- and 2-ethylindoles, indole, and a number of unidentified compounds in different ratios. The yield of indole did not exceed 66%.

The dehydrogenation of THI with the use of palladium-containing catalysts on γ-Al_2O_3 and Sibunithave been briefly mentioned [11]. The yield of indole was quantitative, but it was determined by GLC, which provides no possibility to establish the content of high-boiling admixtures in the major product.

The dehydrogenation of THI on catalysts containing sulfidated palladium or a mixture of oxides (Cr_2O_3, La_2O_3, K_2O) deposited on γ-Al_2O_3 and Sibunit at 360–480°C has been described [12]. Indole was obtained in quantitative yield, although it was the yield of liquid catalyzate that was given in the experimental section. However, the stability of THI and indole at such high temperatures is not typical.

With the aim to develop a technologically feasible method for indole preparation, we have carried out a systematic study whose results are briefly expounded in [13, 14]. The use of nickel sulfide deposited on γ-Al_2O_3 provides the dehydrogenation of THI into indole in 96% yield and a selectivity close to 100%.



The catalyst was obtained by impregnation of γ-Al_2O_3 with an aqueous solution of a nickel salt (chloride or acetate) followed by treatment with a hydrogen sulfide excess or an aqueous solution of alkali metal (or ammonium) sulfide (or hydrosulfide).

In continuation of these studies, we developed an improved catalyst for the dehydrogenation of THI into indole. The catalyst was obtained in an aqueous suspension containing nickel chloride, sodium sulfide,

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granulated aluminum oxide, hydrochloric acid, and a surfactant at ambient temperature.

A substantial difference of the new catalyst from those described in [13, 14] consists in the use of a surfactant for its preparation. This provides the purification and efficient wetting of the aluminum oxide surface, which facilitates the penetration of active components of the catalytic system into granules of the catalyst and their uniform distribution over the support surface. Commercial long-chain sulfonates, for example, sodium dodecylsulfonate, can be used as surfactants.

In the course of preparation, the catalyst is doped with Na^+ and Cl^- ions; the resulting suspension is filtered without washing and then heated in air at 100°C for 20 h. The optimal content of Na^+ and Cl^- ions is within 0.1–0.2 and 0.2–1.0%, respectively. The doping extent can be varied by varying the strength of pressing of catalytic mixture in the course of filtration.

It is reasonable to consider that NaCl and $NaOCl_2$ microcrystals increase the polarization of amphoteric aluminum oxide molecules, thus enhancing the affinity of nickel sulfide microcrystals toward support mesopores. As a result, the mechanical strength and activity of catalyst increase.

The catalyst contains 0.30–2.00% Ni, 0.20–1.50% S, 0.1–0.20% Na, and 0.20–1.00% Cl.

The catalyst is obtained as follows. First, an aqueous suspension containing 10–50% Al_2O_3, 0.3–5% $NiCl_2$, and 0.1% surfactant is obtained under vigorous stirring for 15–60 min. A 36% aqueous HCl solution is added to the stirred suspension to pH 1–3, and then an equimolar amount (with respect to $NiCl_2$) of $Na_2S \cdot 9H_2O$ in an aqueous solution (concentration of 1–15%) is added over a period of 30 min. The suspension is stirred for another 30 min, allowed to stand overnight, then filtered, and heated for 20 h at 100°C.

The catalyst can be readily regenerated by heating at 370°C for 10 h in air.

It is substantial that the new catalyst provides a possibility to carry out THI dehydrogenation to give indole without the use of hydrogen or an inert gas carrier but only in a solvent vapor flow (toluene, petroleum ether, gasoline).

Thus, we have developed the new catalyst of THI dehydrogenation into indole that allows the preparation of the latter in a yield up to 96% and selectivity of 100%.

EXPERIMENTAL

Catalyst preparation. The catalyst was obtained using commercial aluminum oxide γ-Al_2O_3 with a specific surface of 200 m^2/g and granule size 3 × 5 mm.

A mixture of 50 g of γ-Al_2O_3 and 0.1 g of surfactant in 100 mL of distilled water was stirred vigorously for 30 min, then 2.47 g (1%) of $NiCl_2 \cdot 6H_2O$ was added and stirred for 30 min. A 2-mL portion of an HCl solution (36%) was added and stirred for another 30 min. With continuous stirring, a solution of 2.5 g of $Na_2S \cdot 9H_2O$ in 50 mL of distilled water was added over 30 min. After stirring for 5 h, the resultant suspension was allowed to stand overnight, filtered, and dried (100°C, 20 h) to give 52.1 g of the catalyst containing 97.98% Al_2O_3, 0.99% Ni, 0.65% S, 0.10% Na, 0.28% Cl.

Dehydrogenation of THI into indole on the freshly prepared catalyst. A reactor as a vertical quartz tube 10 mm in diameter and 38 cm long with external tunable heating was charged with 4.6 g (9 cm^3) of the catalyst and heated at 370 °C in a nitrogen flow (8.0 L/h) for 5 h. At the same temperature, 0.5 g of THI dissolved in 10 mL of toluene was passed through the reactor during 4 h. Toluene was distilled off from the condensate to give 0.46 g of indole containing 2% of THI (according to GLC data). No other admixtures were found. The yield of indole was 94%, selectivity was 100%. Indole, mp 53.0°C (from hot water); lit. mp 52.5°C [15].

Dehydrogenation of THI into indole on regenerated catalyst. A solution of 0.25 g of THI in 10 mL of toluene was passed for 5.5 h through the same portion of the catalyst, 4.6 g (9 cm^3), worked during 89 h under the same conditions. Toluene was distilled off from the condensate to give 0.23 g of indole. No THI and other admixtures were detected (according to GLC). The yield of indole was 96%, and the selectivity was 100%.

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