Colloid and Nanosized Catalysts in Organic Synthesis: XVI. Continuous Hydrogenation of Carbonitriles Catalyzed by Nickel Nanoparticles Applied on a Support


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Abstract—Conversion of the starting nitriles and selectivity of the products formation during continuous hydrogenation of various nitriles catalyzed by Ni0/Ceokar-2 have been studied as functions of temperature. Performing the process at temperature 120–260°C has led to the formation of a mixture of products containing di- and trialkylamines as well as the corresponding imines and enamines.

Keywords: catalysis, nanoparticles, nickel, hydrogenation, nitrile, amine

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Hydrogenation of nitriles is a widely used method of industrial-scale preparation of different amines applied in pharmacology as well as in textile, agricultural, and polymer industries.

Hydrogenation (including industrial-scale) of nitriles affording primary amines is performed using Ni- and Co-containing catalysts [2–4]. To avoid the formation of side products (secondary and tertiary amines), the process is performed under the elevated pressure of hydrogen or in the excess of ammonia, due to the high reactivity of the formed intermediates, imines and enamines [5]. For example, hydrogenation of nitriles of lauric acid (30 min, room temperature, 2 MPa) using supported nickel catalysts has yielded n-dodecylamine with selectivity 98–99% at the nitrile conversion 60–90% [6].

Hydrogenation of nitriles at Pt- and Pd-containing catalysts generally yields di- and trialkylamines [7, 8]. For example, secondary and tertiary amines have been prepared using Pt and Pt–Pd (1–2 wt %), supported on modified mesoporous silicate carriers (135–175°C, atmospheric pressure), the nitrile conversion being 33–50%; the selectivity with respect to the formation of the tertiary amine was up to 70% [9].

Hydrogenation of different nitriles in a liquid phase using colloid nickel and cobalt as catalysts has been earlier performed [10, 11] (solution in isopropanol, bubbling with hydrogen, 60–70°C, 10–16 h). Secondary amines have been predominantly obtained using the nickel catalyst, whereas the cobalt catalyst has afforded primary amines. The selectivity has been found dependent on the method of the catalyst preparation.

This study aimed to investigate the process of hydrogenation of aliphatic and aromatic nitriles in a flow-through reactor using the catalysts based on Ni0 nanoparticles applied onto various supports, namely γ-Al2O3, activated carbon BAU-A, and aluminosilicate cracking catalyst Ceokar-2 containing 10 wt % of zeolite NaY and up to 1.8 wt % of La2O3 (the rest being SiO2) [12].

The catalysts were prepared via impregnation of the supports with an aqueous solution of nickel(II) chloride, followed by separation of the impregnated support via filtration and reduction of the nickel ions with aqueous solution of sodium borohydride as described in [1].

To study the activity of the prepared catalysts in the nitriles hydrogenation, we performed gas-phase hydrogenation of pentanenitrile at 180°C and atmospheric
pressure, the hydrogen feeding rate being 0.75 L h\(^{-1}\) g\(_{\text{cat}}\)\(^{-1}\) and that of the nitrile being 0.9 mL h\(^{-1}\) g\(_{\text{cat}}\)\(^{-1}\). The secondary amine was the major hydrogenation product using the \(\text{Ni}^{0}/\text{Ceokar-2}\) catalyst (selectivity 74% at the nitrile conversion 83%). When \(\text{Ni}^{0}/\text{BAU-A}\) or \(\text{Ni}^{0}/\gamma\text{-Al}_{2}\text{O}_{3}\) was used as the catalyst a significant fraction of unsaturated compounds was formed, the selectivity of the secondary amine formation being in both cases 30% at the nitrile conversion 35–40%. The study of the catalysts durability revealed that the \(\text{Ni}^{0}/\text{Ceokar-2}\) one retained the catalytic activity during at least 15 h of the process, whereas \(\text{Ni}^{0}/\gamma\text{-Al}_{2}\text{O}_{3}\) and \(\text{Ni}^{0}/\text{BAU-A}\) were deactivated within 5 and 2 h, respectively. The deactivation of metal catalysts during hydrogenation of nitriles is due to the chemisorption of nitriles or imines at their surface [13–16]. In view of the stability, the \(\text{Ni}^{0}/\text{Ceokar-2}\) catalyst was chosen for further investigation.

The surface of the \(\text{Ni}^{0}/\text{Ceokar-2}\) catalyst was studied by means of SEM. As seen in Fig. 1, the support surface was covered by large (200–1000 nm) nickel agglomerates (Fig. 1a) formed of the smaller particles as well as by smaller (80–100 nm) particles (Fig. 1b). It was found that the average content of nickel at the surface equaled 7 wt %; the smaller agglomerates (Fig. 1b) contained 7% of nickel, and larger agglomerates (Fig. 1a) contained 11% of nickel.

To investigate the effect of temperature on the composition of the reaction mixture during hydrogenation on the \(\text{Ni}^{0}/\text{Ceokar-2}\) catalyst, we studied the reaction of different nitriles: \(n\)-pentanenitrile \(1\text{a}\), \(n\)-butyronitrile \(1\text{b}\), isobutyronitrile \(1\text{c}\), propionitrile \(1\text{d}\), and benzo-nitrile \(1\text{e}\). The reaction was performed at temperatures 120–260°C and atmospheric pressure, at constant feed of the nitrile and hydrogen.

The obtained mixtures were analyzed by gas-liquid chromatography and chromat–mass spectrometry. The products composition coincided with the scheme of transformations during nitriles hydrogenation discussed in the literature [2]. In particular, the reaction mixture contained secondary \(3\text{a}–3\text{e}\) and tertiary \(5\text{a}–5\text{e}\) amines as well as the corresponding imines \(2\text{a}–2\text{e}\) and enamines \(4\text{a}–4\text{d}\) (Scheme 1).

The study of the conversion of nitrile \(1\text{a}\) and the selectivity of formation of amines \(3\text{a}\) and \(5\text{a}\), imine \(2\text{a}\), and enamine \(4\text{a}\) as functions of temperature revealed that the increase in the hydrogenation temperature led to linear increase in the conversion, the selectivity of the process remaining practically constant. The highest conversion of nitrile \(1\text{a}\) was 83% at 200°C, the selectivity being equal 74% with respect to the secondary amine \(3\text{a}\) and 20% with respect to the tertiary amine \(5\text{a}\) (Fig. 2).

In the case of nitrile \(1\text{b}\), the conversion became constant (close to quantitative yield) at temperature above 200°C. The highest conversion of nitrile \(1\text{b}\) was 99% at 260°C, the selectivity equaled 64% with respect to di-\(n\)-butylamine \(3\text{b}\) and 13% with respect to tri-\(n\)-butylamine \(5\text{b}\). The formation of intermediate hydrogenation product enamine \(4\text{b}\) was observed. The selectivity of the formation of the secondary amine \(3\text{b}\) increased with temperature (Fig. 3).