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The effect of copper on benzene hydrogenation to cyclohexane over Ni/Al_2O_3 catalyst

Kamila Michalska[a], Paweł Kowalik[a,*], Marcin Konkol[a], Wiesław Próchniak[a], Kazimierz Stołecki[a], Grzegorz Słowik[b], Tadeusz Borowiecki[b]

[a] *New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13A, 24-110 Puławy, Poland*
[b] *Marie Curie-Skłodowska University, Faculty of Chemistry, Department of Chemical Technology, pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland*

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ABSTRACT

The effect of a copper modifier on physicochemical properties of coprecipitated precursors and final Ni–Cu/Al_2O_3 catalysts for benzene to cyclohexane hydrogenation was investigated. Based on the studies of physicochemical properties, the influence of copper on the catalytic activity and selectivity of Ni–Cu/Al_2O_3 systems was discussed. The addition of copper resulted in a decrease of the specific and nickel surface area, improvement of the selectivity and a slight decrease of the benzene hydrogenation activity compared to the reference catalyst. A decrease of methylcyclopentane and methylcyclohexane by-products formation on the surface of Ni–Cu/Al_2O_3 catalyst containing 10–17 wt% CuO by, respectively, 70% and 10% was observed. The results reveal a distinct, beneficial effect of the Ni/Al_2O_3 modification by copper on the catalyst selectivity. However, this effect depends on temperature and is limited to ca. 20 wt% CuO, above this content the activity was found to decrease considerably.

1. Introduction

The catalytic hydrogenation of benzene to cyclohexane is one of the stages in caprolactam production process [1,2]. Due to the high exothermic effect, the process is usually carried out in a series of two tubular reactors thermostated with boiling water. In the first stage the process runs under hydrogen lean conditions, at pressures in the range 0.2–0.3 MPa. Such conditions allow the maintenance of the process temperature in the range up to 250 °C and hamper the hydrogenolysis of benzene to methane and formation of other byproducts (methylcyclopentane – MCP, methylcyclohexane – MCH) that in consequence leads to higher hydrogenation selectivity. The second stage is carried out under hydrogen-rich conditions, at pressures in the range 0.6–1.2 MPa, resulting in a high degree of benzene conversion [2].

The Ni/Al_2O_3 or Ni/SiO_2 catalysts [3] with a relatively high content of nickel oxide (40–60 wt%), in the form of pellets, balls or extrudates are most often applied in the industrial practice. The requirements for benzene hydrogenation catalyst include high activity, mechanical strength, stability and coke resistance. These features depend on the nickel content [4] and dispersion [5], addition of promoters, support type [6–9] and preparation technique [10]. A particular requirement for benzene hydrogenation catalysts is their high selectivity. In the literature there have been many contributions indicating some possibilities of the selectivity improvement via an addition of promoters to nickel catalysts. Moreover, the literature data indicate a beneficial effect of copper on the selectivity of Ni/Al_2O_3 catalysts in the benzene hydrogenation reaction [11–13]. However, these reports concern most of all catalysts prepared by means of impregnation techniques. There have been also several interesting contributions on Ni–Cu–Al catalysts from coprecipitated hydrotalcite-like precursors and their assessment in other hydrogenation reactions [14–17]. However, to the best of our knowledge, there have been no studies on coprecipitated Ni–Cu–Al systems in terms of the benzene to cyclohexane hydrogenation. The contributions dealing with benzene hydrogenation on Ni and Ni–Cu catalysts focus on selectivity towards cyclohexane and methane [5,18]. The problem of other byproducts formed in benzene to cyclohexane hydrogenation reaction (MCP, MCH) has been discussed in literature very sparsely.

The main goal of this contribution is to determine the effect of Cu addition on catalytic and physicochemical properties of Ni–Cu/Al_2O_3 catalysts for benzene hydrogenation prepared via co-precipitation route. The catalytic features (activity and selectivity) of several systems with a various Cu/Ni ratio have been compared

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* Corresponding author.
E-mail address: pawel.kowalik@ins.pulawy.pl (P. Kowalik).

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and the modifier role in the benzene hydrogenation reaction has been tentatively proposed.

2. Experimental

2.1. Preparation of catalysts

A series of model catalysts with a varying content of NiO (50–80 wt%), CuO (0–36 wt%) and Al_2O_3 was prepared. The catalysts precursors were obtained by means of co-precipitation from a solution of nickel nitrate (or nickel and copper nitrates), with a solution of sodium aluminate and sodium carbonate. The synthesis of precursors was carried out in a continuous mode, in the pH range 7–7.5 and at the temperature of 70–80 °C. The precipitates were washed with distilled water to achieve filtrate conductivity below 300 μS. After drying, the precursors were calcined at 400 °C for 4 h, formed into tablets and crushed. The fraction of 0.16–0.25 mm was then sieved.

2.2. Methods

The chemical composition of the catalysts was determined by means of the XRF method using a X'Unique II Philips spectrometer. The XRD measurements were performed on a PANalytical Empyrean system (Bragg-Brentano geometry) equipped with a PIXcel^{3D} detector, using Cu Kα radiation ($\lambda = 1.542$ Å) and operating at 40 kV and 40 mA. The samples were scanned between $10 < 2\theta < 70°$, with a step size 0.053° and time/step of 30 s. The TPR measurements were performed using AutoChem 2950HP Micromeritics system. The catalysts samples were dried in a helium stream (20 ml/min) at 200 °C for 30 min. The samples were then cooled to ambient temperature and activated with hydrogen (40 ml/min), increasing the temperature with a rate 10 °C/min. The reduction process was monitored using TCD by measuring the signal of water vapor that was a product of the reduction of copper and nickel oxides [19]. The specific surface area of the samples was determined with nitrogen adsorption isotherms at the temperature of liquid nitrogen (−196 °C) and in the p/p_0 range 0.05–0.3 using an ASAP 2050 Micromeritics analyzer. The nickel active surface area (S_{Ni}) was determined by hydrogen chemisorption at 35 °C using an ASAP 2020 Micromeritics analyzer assuming Ni/H = 1 chemisorption stoichiometry. The chemisorption experiments were carried out for the catalysts reduced with hydrogen at 400 °C for 2 h.

The average nickel crystallites size was determined by means of two methods:

- from the chemisorption measurements using the equations: $S_{Ni}[m^2/g] = n_H \times N_A \times A_V \times m^{-1} \times X_{Ni}{}^{-1}$ (1) and $d_{chem}[nm] = 6 \times 10^3 \times \gamma_{Ni}{}^{-1} \times S_{Ni}{}^{-1}$ (2), where: n_H—H_2 adsorbed [mol], N_A—Nickel atom area ($6.45 \times 10^{-20}\ m^2/at_{Ni}$), A_V—Avogadro number [at/mol], γ_{Ni}—nickel density [g/cm^3], S_{Ni}—active nickel surface area [m^2/g_{Ni}], m—sample weight [g], X_{Ni}—nickel content [wt.%].
- from FWHM (full width at half maximum) of the peak at the 2θ angle of 44.4°, corresponding to the Ni (111) plane, according to the Scherrer equation $d_{XRD} = k \times \lambda \times (\beta \times \cos\theta)^{-1}$ (3) [20], where: k—Scherrer equation constant (0.9), λ—wavelength of radiation [nm], β—line broadening of the XRD peak (FWHM) [rad], θ—diffraction angle [rad].

The surface composition of the catalysts was determined by the XPS method in a multichamber UHV Prevac system. The samples were reduced in hydrogen at 400 °C for 2 h before measurements. The XPS spectra were collected using Scienta R4000 photoelectron analyzer equipped with an aluminum anode (132 W) and a CCD/MCP detector. The XPS spectra were processed using a CasaXPS application. The background signals in spectra were evaluated by means of Shirley algorithm, and the contents of particular elements with CasaXPS based on the peak areas, taking into account background and relative sensitivity factors (RSF) for particular lines. The energy scale of spectra was calibrated at a position of Ni2p 3/2Al peak for binding energy of metallic nickel that was 852.8 eV.

The high-resolution electron microscope Titan G2 60–300 kV (FEI Company), equipped with the field emission gun (FEG) was used to display the catalysts. Microscopic studies of the catalysts were carried out at an accelerating voltage of the electron beam equal to 300 kV. Phase separation (Cu, Ni and Al_2O_3) was performed with the FFT by using a masking available in the Gatan Digital Micrograph software package. On the basis of the FFT generated from HRTEM images of the reduced catalysts, individual phases with various crystallographic orientation derived from copper and nickel phase were identified.

The experimental setup for measurements of benzene hydrogenation rate and selectivity is presented in Supporting Information. The key element is a gradientless reactor [21], operating at atmospheric pressure. The reactor was fed with an oxygen-free hydrogen stream, saturated in a thermostatic vessel with benzene or benzene/cyclohexane vapors. The reaction products were separated from the effluent gas and then analyzed by means of refractometry and chromatography.

The benzene hydrogenation rate was determined in the temperature range 180–220 °C at space velocities (4–6 Ndm^3/h) of reaction mixture ($C_6H_6/C_6H_{12}/H_2$ [% mol]: 10/0/90) at the degree of conversion of ca. 50%. The evaluation of the reaction selectivity was carried out at space velocity 4 Ndm^3/h at the temperature 260 °C, feeding the reactor with hydrogen saturated with benzene/cyclohexane vapors of the ratio close to equilibrium value. This approach allowed the measurements at a constant benzene/cyclohexane ratio, independently of the catalytic activity (the main reaction was in equilibrium, only side reactions occurred). The reaction selectivity was expressed as a ratio of the byproducts formation rate (MCP or MCH) to the benzene hydrogenation rate; r_{MCP}/rC_{6H6} and r_{MCP}/r_{C6H6} respectively.

The catalysts were activated with hydrogen during heating up to 400 °C and then stabilized for 4 h. The temperature was then decreased to 180 °C and the reactor was fed with the reaction mixture. Upon reaching of the operating conditions, the liquid products were condensed and their composition was analyzed using a Shimadzu 2010Plus GC. The catalysts were stabilized for 1 h before each activity and selectivity measurements. The stability of the catalytic activity and selectivity of the copper-free ($0Cu/Al_2O_3$) and $Ni–Cu/Al_2O_3$ ($0.25Cu/Al_2O_3$) catalysts was determined in an analogous way by monitoring these parameters for 24 h.

3. Results

The XRF results of the chemical composition and the physicochemical features of the catalysts under study such as specific surface area, Ni surface area and average nickel crystallite size determined by means of XRD (d_{XRD}) and chemisorption methods (d_{chem}) are presented in Table 1.

The results confirm a good agreement between actual and nominal composition and indicate that a series of catalysts with a various Cu/Ni ratio and almost the same Al_2O_3 content were prepared. They reveal that the specific surface area and Ni surface area of catalysts depend on Cu/Ni ratio. Both were found to decrease with the increasing Cu/Ni ratio, albeit for the Ni surface area this trend was more distinct as can be observed from a decrease of the chemiosorbed hydrogen on the catalyst surface (Fig. 1).