The Effects of Modifying the Catalytically Active Phase Through Ni Impregnation of the Cu-Ru Catalyst on Carbon Support in Nitrobenzene Hydrogenation

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We report herein on the hydrogenation of nitrobenzene over 5%Cu-1%Ru/C and 5%Cu-1%Ru-8%Ni/C catalysts respectively, using a pilot laboratory installation and their performances in order to outline the effect of Ni addition in the Cu and Ru-based catalyst. The experiments were performed on beds of catalyst extrudate, with a volume of $40\ cm^3$, for a range of temperatures from 45 to 75°C, pressures from 1 to 4 MPa, space velocities from 0.2-$0.6h^{-1}$, feed ratio $H_2/C_6H_5NO_2=10/1mol/mol$. The performances were evaluated based on conversion values of nitrobenzene and the yields of the most significant reaction products, both of which were assessed through analyses of raw materials and reaction products by GC-MS. Although Ni is widely known as a common catalyst for hydrogenation, we have established the inhibitory effect of Ni addition on the Cu-Ru/C catalyst obtaining, in some cases lower total conversions, but having a potent effect on modifying the selectivity of reaction products, with a quantitatively varying effect depending on working pressure.

Keywords: Nickel, Copper, Ruthenium, active carbon, nitrobenzene, selectivity, active phase, catalytic support, inhibitor

The use of aniline obtained through nitrobenzene reduction has numerous applications, as we have previously demonstrated [1,2]. Furthermore, among methods of obtaining aniline from nitrobenzene, one of the most important is catalytic hydrogenation. This method permits the generation of large quantities of reaction products, in conditions controlled by operating parameters, with zero to minimum residual products which either are pollutants or difficult to valorize. Finding a catalytic system with maximum catalytic performance remains an ongoing quest, although there are numerous studies which concern achieving the reaction of nitrobenzene hydrogenation using a variety of catalytic systems. The catalytically active substances for the hydrogenation of the nitro function in the studied catalytically systems have been, by and large, in metallic form [3].

Initial investigation in the field were carried out on type Pd/C catalysts [3]. In this case, it was established that the reaction is sensitive to/with the nature of the solvent, and that of the carbon-based/*carbonaceous* support [3]. Evidently, due to their technological advantages, the most used catalytic systems have been those obtained through the impregnation of supports with solutions of catalytic active phase precursors [12], however the studies on alternative systems such as Ni Raney are not negligible [3]. Among the catalytic systems previously investigated are those with Pt on supports [4], Pd on various supports [3,4], Ni on various supports [3,5], Cu on supports [3]. One of the much-studied active elements is Ru deposited on various supports [6-11]. These catalytic systems previously described exhibit differences regarding mainly supports, and the results obtained reflect differences in their performance. Thus, support can be active carbon [6,8], SBA-15 [7], Ru deposited on silica or alumina [8].

Previous studies were performed on multimetallic systems, *i.e.* bi- and trimetallic systems [3,9,10]. The characterization of these catalysts was performed in order to establish if there is a correlation between surface properties and the nature of putative/possible/potential metal-metal interactions. Previous work [9-10] suggests that on the surface of supports metallic particles with mixed composition can form when such multimetallic systems are employed [3]. If on the one hand type Ni/supports monometallic systems have proven very effective in the hydrogenation of benzene [11], the nickel layed/deposited on species of titanium dioxide (rutile, anatase and large surface titania) achieving conversions of over 90% at work temperatures of 140 and 150°C [9], on the other hand, with multimetallic systems the addition of nickel can generate interactive effects with other active species which can lead to either an increase or decrease of catalytic performance [12]. The ruthenium-based catalyst modified with copper on active carbon support proved to be active in nitrobenzene hydrogenation [1]. In turn, monometallic systems with an active phase composed of copper or ruthenium or nickel on active carbon [1,6,9] have proven to be active, as well, in the hydrogenation of nitrobenzene, however the activity differs from one system to the other.

The present paper sets out to determine the effects of Ni addition on the principal catalytic properties of the metals which comprise the active phase, by comparing the trimetallic system Cu-Ru-Ni/C with the bimetallic system Cu-Ru/C, for the hydrogenation of nitrobenzene.

Experimental part
Materials and methods
Precursor salts of catalytic active agents were used for the synthesis of catalyst: *Ruthenium* (III) *chloride trihydrate* (Sigma-Aldrich), copper nitrate *trihydrate* (Sigma-Aldrich), nickel (II) nitrate hexahydrate (Sigma-Aldrich). Granular activated carbon (Merck) was used for the support preparation. The carrier gas, activation and hydrogenation gas was electrolytic hydrogen (Linde). Nitrobenzene ACS reagent was used (Merck), diluted with *n*-heptane of analytical grade (Merck).

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Two types of catalysts: 1%Ru-5%Cu/C granular activated carbon and 1%Ru-5%Cu-8%Ni/C granular activated carbon were prepared by the support impregnation with precursor aqueous solutions salts of metals from the active phases. Ruthenium deposition was performed by the pore volume impregnation method, with aqueous solutions of *ruthenium (III) chloride trihydrate [13] and Cu and Ni deposition by the i*ncipient wetness impregnation method, with aqueous solutions of copper nitrate *trihydrate and* nickel (II) nitrate hexahydrate [13].

The chemical composition of the catalysts was determined by atomic absorption spectroscopy. Some physical characteristics of the support were determined: the value of bulk density of support granules (carbon Merck), a textural analysis of the support by using the analysis of the adsorption isotherm of the carbon granules Merck.

The hydrogenation of nitrobenzene on the bimetallic catalytic systems Ru-Cu/C and trimetallic catalytic systems Ru-Cu-Ni/C was performed in a pilot laboratory scale installation provided with a tubular metallic reactor with descending flow rate of raw material and hydrogen and isotherm regime.

The feed of liquid raw materials with nitrobenzene 50% diluted with n-heptane 50% (vol.) was performed with dosing pump (HPLC type) and hydrogen was introduced from a pressure gas cylinder provided with pressure adjustment regulators and flow rates.

The installation was equipped with a condenser and phases separator for liquid and gases products.

The cylindrical metallic reactor is electrically heated and is equipped with temperature and pressure measurement and adjustment devices, with the following geometrical characteristics: reactor height (H): 500 mm; the reactor inner diameter (D): 25 mm; the ratio (H/ D): 20/l; flowing section: 440 mm^2; the reactor volume: 200 cm^3; the maximum catalyst volume: 100 cm^3.

The catalytic performances of the two systems were determined in the micro pilot laboratory installation, in the following experimental conditions: molar ratio $H_2/ C_6H_5NO_2$ 10:1; pressure 4 ; 2.5 ; 1 MPa; operating temperature: 45, 55, 65, 75°C; volume flow rates: 0.2 h^{-1}, 0,4 h^{-1}, 0,6 h^{-1} .

For the liquid product, the reagent conversions and the reaction products yields were calculated based on the material balance and the chromatogram of the collected liquid.

The analysis of raw materials and liquid samples was performed by using a gas chromatography-mass spectrometry (GC-MS) method, with a VARIAN type gas-chromatograph coupled with a mass spectrometer.

The column of the components separation was a capillary type with stationary phase VF-5ms, length of 30m, inner diameter of 0.25mm and film thickness of 0.25μm.

The operating conditions of GC-MS were kept constant during all samples analyses.

The other parameters of GC-MS method were the following: the injector temperature 300°C, flow rate of the eluent (carrier gas) 2mL/min, splitting ratio 1:50; carrier gas - helium; detector MS; the ion source temperature: 300°C; interface temperature 300°C; MS mode EI.

Experimental data were collected by using the device software and the identification of the compounds was achieved by comparing mass spectra of these chemical compounds to those of Mass Spectral Library of the software (NIST147 and NIST27). After performing the analyses, the following compounds were identified: nitrobenzene, n-heptane, aniline, N-methylaniline, diphenylamine, diphenylhydrazine, azobenzene, nitrocyclohexane.

Results and discussions

Nitrogen adsorption-desorption isotherm at 77K is presented in figure 1, the plot volume adsorbed obtained by measuring the amount of N_2 gas that adsorbs onto the surface of interest (cm^3/g) and the relative pressure (p/p_0), for the relative pressure interval of 0 to 1 and 1 to 0.
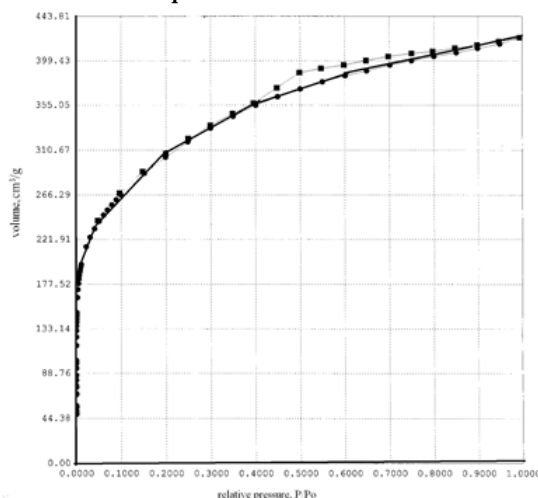

Fig.1. Nitrogen adsorption-desorption isotherm on carbon granules Merck, at normal boiling temperature of nitrogen (77 K)

The support is rich in micropores, their volume is under the domain of hysteresis loop, followed by the region of mesopores in the domain of hysteresis loop and then the region of macropores, with the smallest content.

Thus, it was established that the value of bulk density of support granules (carbon Merk) was 0.449 g/cm^3, the specific surface area of the support was 487 m^2/g. The hysteresis loop was analyzed and it resulted that those are H4 type (fig. 2), comparing to H1-H4 hysteresis types presented in literature [12]. This type corresponds to some narrow pores placed between two horizontal plates.
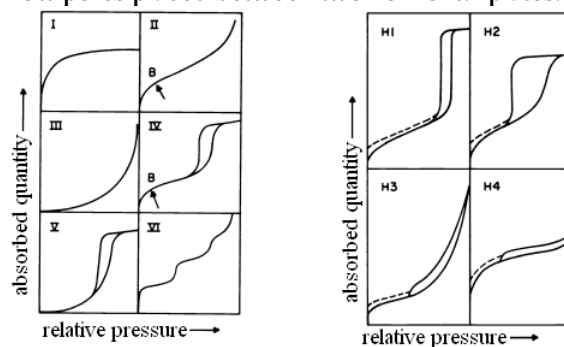

Fig.2. Types of adsorption isotherms and hysteresis loops types

After performing a preliminary experimental program, at 45°C and 4 MPa, we observed that the highest conversions were achieved on the interval of investigated volume rates of 0.2 h^{-1}, for all catalytic systems.

The influence of temperature and pressure on the catalytic performances of the two systems was studied at the value of volume rate 0.2 h^{-1}. The hydrogenation conversion of the studied reagent, calculated as a ratio between the quantity of nitrogen transformed in all the reaction products from the collected liquid and the quantity of nitrogen fed during the experiment was studied for the four temperatures which were mentioned, at different work pressures: 4; 2.5 and 1 MPa. The values of conversion for the different reaction temperatures were in domains which varied with the experimental pressure. It was observed from figure 3 that conversions were between 30 and 80%, approximately the same for the two catalysts used in the experiments.
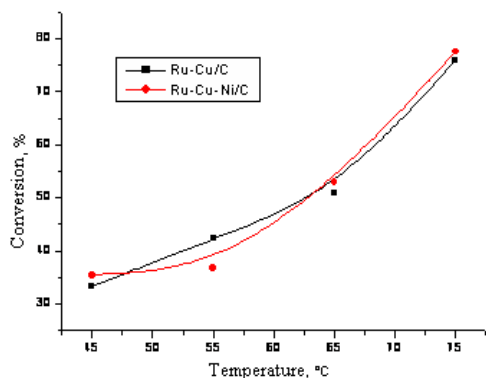
Fig.3. The variation of the conversion with temperature for the hydrogenation of nitrobenzene over Ru-Cu/active C and Ru-Cu-Ni/ activated C catalysts; Working pressure 4MPa, volumetric flow *rate* 0.2h⁻¹

Different behaviors were observed at the experimental pressure 2.5 MPa (fig.4). The highest conversion of the experimental program was obtained: value greater than 90% to almost 100%.

The addition of nickel to the system Ru-Cu/active C inhibited the action of the catalytic couple, at these pressure experimental values. The differences of 1-2 percent were favorable for the binary system, comparing to the ternary system, these values being not significantly.
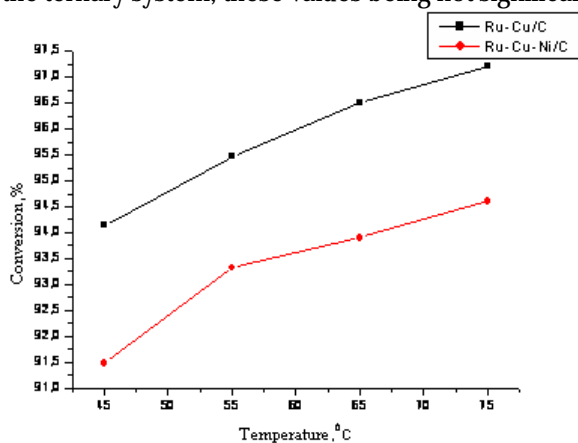

Fig.4. The variation of the conversion with temperature for the hydrogenation of nitrobenzene over Ru-Cu/active C and Ru-Cu-Ni/ activated C catalysts; Working pressure 2.5 MPa, volumetric flow rate 0.2h⁻¹

For the experiments performed at pressure of 1 MPa (fig.5), the values of conversion in function of temperatures are low, even lower than those registered at pressure of 4 MPa, between 2% and almost 30%. For these values of pressure, the conversions which were obtained by using the catalyst with addition of nickel at Ru-Cu/active C were higher than those which were obtained with the binary system, on the whole interval of reaction temperatures.

Significantly concentrations of the reaction products were observed from the gas - chromatography analysis of the liquid product which was collected after the condensation system, these values being different as a function of the catalytic system used and operating conditions. It is important to mention that besides aniline, the main reaction products are hydrogenation-condensation products. In less severe conditions of temperature, when condensation is not very important to form insignificant reaction products, more numerous reaction compounds were obtained. The apparent lack of reaction by-products from the liquid collected at reaction temperatures higher than 55°C may be due to the age of
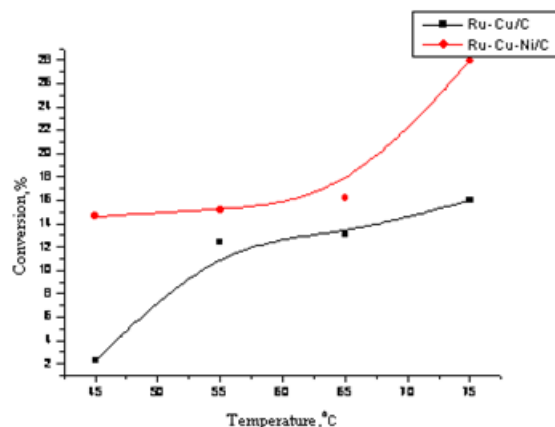

Fig. 5. The variation of the conversion with temperature for the hydrogenation of nitrobenzene over Ru-Cu/active C and Ru-Cu-Ni/ active C catalysts; Working pressure 1 MPa; volumetric flow rate 0.2h⁻¹

some advanced condensation products, that remain irreversibly adsorbed or they can not be determined by the gas-chromatographic method. Thus, the main product, aniline, reach maximum concentration in the reaction liquid at the maximum temperature experienced and working pressure of 2.5 MPa (fig. 6). This figure shows also a process favoring the ternary system (Ru-Cu-Ni/C), comparing to the binary system (Ru-Cu/C), meaning that yields of aniline obtained on the ternary system exceeds the entire operating pressure range than the yield obtained for the binary system. This suggests that the ternary system would have greater selectivity in the main hydrogenation product (aniline) and although apparently the binary system would therefore have a better activity than the ternary one, the selectivity to aniline will be favored by the addition of Ni to the catalyst Ru-Cu/C.
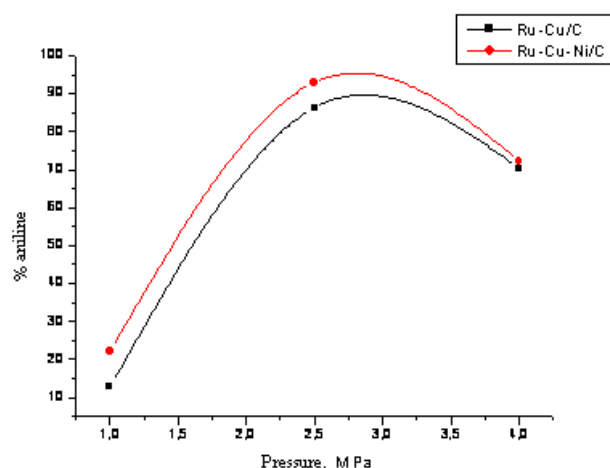

Fig.6. The variation of aniline content in the liquid product as a function of the operating pressure on bimetallic catalyst (Ru-Cu/C) and trimetallic catalyst (Ru-Cu-Ni/C); the reaction temperature 75°C and volumetric flow *rate* 0.2 h⁻¹.

Regarding byproducts, they were obtained especially at low reaction temperatures of 45 and 55°C and operating pressure of 2.5 MPa. These products were the following: N-methyl aniline, diphenylaniline, azobenzene, diphenyl-hydrazine and other unidentified products. Concentrations of byproducts were of the same order of magnitudes for the two catalytic systems.

The reaction temperature increases, as it is known, does not lead to increased main product selectivity and thus to decrease mainly the formation of byproducts, but the increase in contents of unidentified products, possibly advanced condensing compounds.

Conclusions

Two catalytic reaction systems, Ru-Cu/activated C and Ru-Cu-Ni/activated C were prepared in the laboratory by pore volume impregnation method, with aqueous solutions of ruthenium (III) chloride trihydrate for ruthenium and for Cu and Ni deposition by incipient wetness impregnation method [11], with aqueous solutions of copper (II) and nickel (II) nitrates.

The catalysts were characterized by several physicochemical methods: atomic absorption, bulk density, porosimetry by analysis of nitrogen adsorption isotherms.

Textural analyzes revealed that the support was mesoporous, developing a catalytic surface and pore volume in the upper limit of values applied in heterogeneous catalysis.

The analysis of the hysteresis loop shape revealed that it corresponds to the shape of some narrow slit pores created between the horizontal plate packages.

The catalytic performances were determined in a laboratory-pilot plant, working at high operating pressures of 1; 2.5 and 4 MPa, at reaction temperatures of 45, 55, 65 and 75°C.

The experimental program carried out showed that the addition of Ni to the binary system of Ru-Cu/active C does not lead to the increase of the catalytic activity, on the contrary, it appears to partially inhibit the activity at working pressure of 2.5 MPa.

The conversions achieved were more than 90% for the binary and the ternary system, over the entire operating temperature range, lower for the ternary system than the binary one.

The aniline selectivity was favored by the addition of Ni to the catalytic system of Ru-Cu / C.

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