Nitrobenzene Hydrogenation over Catalysts Cu based Supported on Activated Charcoal

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Hydrogenation of nitrobenzene to amino aromatics was performed using catalysts Cu based supported on charcoal. Experiments were performed in a continuous sistem and fixed bed reactor at a pressure of 10 – 40 bar, and a temperature of 45 -75 ^{0}C, with a weight hourly space velocities of nitrobenzene of 0.2 – 0.6 h^{-1}and a molar ratio hydrogen / nitrobenzene of 10; nitrobenzene was diluted in n-heptane. Acid strength distribution of the two catalysts (1.5% Ru-5% Cu activated carbon and 5% Cu/activated carbon) where determined by termodesorption of diethyl amine. The major compounds identified in the hydrogenation of nitrobenzene were aniline, diphenylamine, diphenylhydrazine, azobenzene and nitrocyclohexane. It was observed that the conversion of nitrobenzene and aniline yield shows a parabolic variation with increasing of pressure, probably due to sintering of the catalyst at higher pressure, which is favored by high exothermicity of the hydrogenation process of nitrobenzene correlated with the increase of the proportion of nitrobenzene in liquid phase.

Keywords : nitrobenzene, catalyst, hydrogenation, support acidity, aniline

Classical method to obtaining of aromatic amines consists in hydrogenation of the corresponding aromatic nitro compounds in heterogeneous catalysis [1-7]. Hydrogenation of nitrobenzene to aniline, an important raw material for synthetic dyes, chemicals, rubber, explosives, agricultural products, resins and polyurethanes, is a much studied, deriving with in the formation of various secondary compounds such as N-fenilhidroxilamina, diphenylamine, diphenylhydrazine, azobenzene, nitrociclohexan. Catalytic systems tested to this process were various.

Thus, Mária Turáková et al [8] prepared two kinds of catalysts Pd / C using different precursors, Na_2PdCl_4, respectively H_2PdCl_4, with different contents of palladium (1-10 wt.%). The high catalytic activity of the catalyst was carried out using 1-4 wt.% palladium.

Hydrogenation of nitrobenzene was carried out on Cu based catalysts. Thus Danilova et al [9] studied the hydrogenation of nitrobenzene to aniline on a copper catalyst supported on a metallic nickel-aluminum distributed on an heat exchanger tube. The catalysts prepared according to the technique proposed have a high thermal conductivity and are active in this process. Thus nitrobenzene conversion increases with increasing copper concentration from 10 to 20% by weight.

Astam Kumar Patra et al [10] proposed a selective chemical solution for hydrothermal synthesis to form the nano-rods with a length of 100-235 nm and nanospheres with a diameter of approx. 14 nm using saturated fatty acids. Copper nanospheres show a catalytic activity improved compared with the nano rods for the reduction of aromatic nitro compounds to anilines substituted, at room temperature. Smaller sizes of particle with higher BET surface area (6.1 toward 1.5 m^2 g^{-1}) could be responsible for higher catalytic activity of nanospheres, suggesting the role of particle size and shape in the catalytic reduction.

Shigang Diao et al [11] studied the hydrogenation of nitrobenzene in the vapour phase over a catalyst Cu/SiO_2 in a fluidized bed reactor in a single stage and in two stage, at 513-553 K and atmospheric pressure. Thus, the conversion of nitrobenzene and the aniline selectivity and stability of the catalyst significantly increased when the process is carried out in a fluidized bed reactor in two stages, in comparison with that in a single step. Advanced Transformation of nitrobenzene with a high selectivity to aniline, and also the flexibility to regenerate of the catalyst are the main advantages of this process.

RAJ K. Joseph Antony et. al. were performed catalytic hydrogenation of nitrobenzene to aniline on the nickel catalyst impregnated with rutile, anatase, and titanium dioxide supports with high specific surface [12]. The order of catalytic activity for the hydrogenation of nitrobenzene was Ni / rutile > Ni / anatase > Ni/TiO_2. For the catalyst Ni /rutile at a temperature of 140°C and a pressure of hydrogen of 1.96 Mpa, was observed a conversion of 99%. On the same catalysts $Ni/\gamma\text{-}Al_2O_3$, Xiangchun Meng et.al. investigated the selective hydrogenation of nitrobenzene using various solvents: CO_2 in the dense phase, ethanol and n-hexane [13]. The total conversion of nitrobenzene hydrogenation was higher in the CO_2 dense phase, than in organic solvents under the similar reaction conditions; selectivity to aniline was about 100% over the range of conversion obtained.

Given the high exothermicity of this reaction, one of the issues relevant to this process is to maintain the desired temperature regime and preventing local overheating of the catalyst to prevent sintering and thus disabling them. From this perspective, the present study evaluates the behaviour of catalysts based on metals with high thermal conductivity such as copper deposited on a substrate with high porosity and low thermal conductivity such as activated carbon in the vapour phase and liquid phase hydrogenation

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of nitrobenzene at high dilutions made through the use of solvents.

Experimental part

The raw materials used in experiments were nitrobenzene analytical grade (Merck), n-heptane of analytical grade (Merck), copper(II) nitrate trihydrate puriss. p.a. (Sigma-Aldrich), ruthenium chloride trihydrate technical (Sigma-Aldrich), granular activated charcoal (Merck) and electrolytic hydrogen purity from Linde Company.

The experimental program was performed in a continuous fixed bed catalytic reactor. The temperature was regulated with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket. A metallic jacket for the mobile thermocouple was also placed in the axis of the reactor, the sheath in which was axially placed in the central zone of the catalyst bed, in order to measure the reaction temperature. The process was carried out in isothermal conditions.

Reaction conditions for catalysts were:

-pressure: 10 – 40 bar;

-temperature: 45 -75^{0}C ;

-weight hourly space velocity of nitrobenzene: 0.2 – 0.6 h^{-1};

-molar ratio hydrogen/ nitrobenzene: 10/1.

Nitrobenzene was redistilled and diluted with heptane, the total content of nitrobenzene in the reaction mixture being 50% by volume. Catalysts used 5% Cu / granular activated charcoal and 1.5% Ru-5% Cu /granular activated charcoal, where prepared in the case of Ru by incipient wetness impregnation method with aqueous solution of ruthenium chloride trihydrate, and in the case of Cu by the pore filling method with aqueous solution of copper nitrate. Chemical composition of the catalyst used in the experimental program was determined by atomic absorption. Acid strength distribution of catalysts where determined by termodesorption of diethyl amine in the temperature range 20-700°C. Thermal analyzes (ATG, DSC) were performed on a DuPont Instruments' Thermal Analyst 2000/2100 "coupled with a module "951 Thermo-gravimetric Analizer" (fig. 1 and fig. 2).

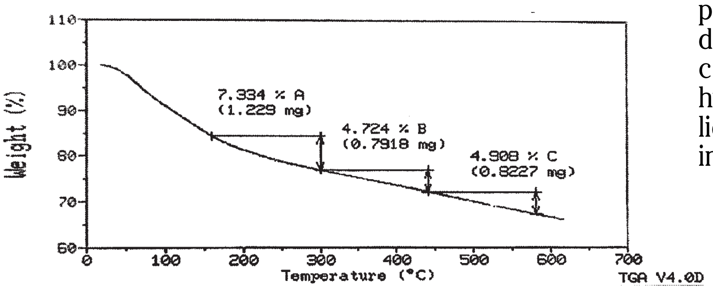


Fig. 1. Acid strength distribution of catalyst 5% Cu / granular activated charcoal catalyst type

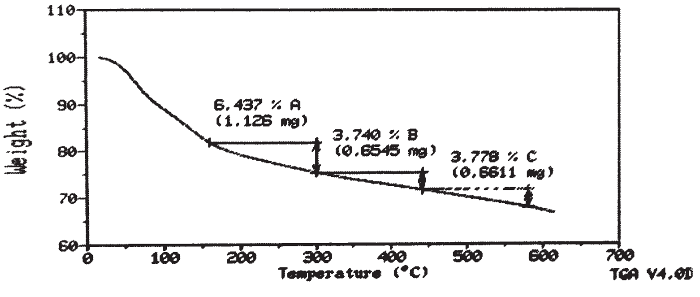


Fig. 2. Acid strength distribution of catalyst 1.5%Ru-5% Cu /granular activated charcoal catalyst type

Catalyst activation was performed „in situ" in the presence of hydrogen at a temperature of 450^{0}C during 6 h.

The composition of the reaction mixture was performed by the method of gas chromatography coupled with mass spectrometry on a Varian CP-3800 chromatograph. MS capillary column was a Varian column MG - 17-15-1, WCOT fused silica with 30 m length. The column used to separate the constituents of reaction mixture was a capillary Varian VF-5 with 30 m length and 0.25 mm internal diameter.

Results and discussions

The catalyst 5% Cu /activated charcoal shows a relatively uniform distribution of the concentration of acidic centers with medium and high acidity, and approximately with 50% higher for the concentration of centers with low acidity. The catalyst 1.5% Ru-5% Cu /activated charcoal shows a lower concentration of acid centers than the catalyst 5% Cu /activated charcoal, concentration of medium and high strength centers being at a concentration of about half that of weak centers.

The major compounds identified at nitrobenzene hydrogenation were aniline, N-methyl aniline, diphenylamine, diphenylhydrazine, azobenzene and nitrocyclohexane. Variation of conversion of nitrobenzene with weight hourly space velocities is shown in figure 3. Note that the process occurs with a decrease in conversion with weight hourly space velocity and the diminution of conversion is more pronounced in the case of 1.5% Ru-5% Cu/ activated charcoal catalyst type.

Variation of nitrobenzene conversion with pressure is shown in figure 4. Note that in the case of the catalyst 1.5 % Ru -5 % Cu /activated charcoal is obtained an conversions greater than in the case of the catalyst 5 % Cu /activated charcoal, for all field of the pressure variation studied. Nitrobenzene conversion curve of pressure is similar for both catalysts, showing values above 90 % for the catalyst 1.5 % Ru -5 % Cu /activated charcoal and 60% for the catalyst 5% Cu /activated charcoal catalyst. Thus the conversion of nitrobenzene increases with pressure for lower values of 25 atm and decreases with increasing pressure above values of 25 atm at both catalysts tested. Decreasing of nitrobenzene conversion with increasing of pressure to values above 25 atm, is probably due to the decrease of catalyst activity as a consequence of sintering catalyst generated by high exothermicity of the hydrogenation process of nitrobenzene to amine in the liquid phase, the growth of pressure favoring the increase in the proportion of nitrobenzene in liquid phase.

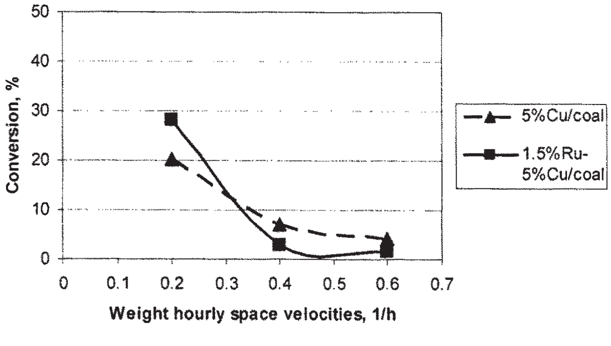


Fig. 3. Variation of nitrobenzene conversion with weight hourly space velocities (40 atm pressure and 40°C temperature)

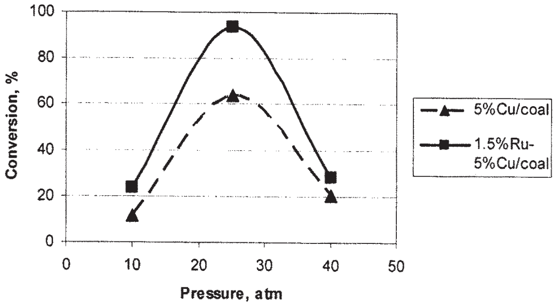


Fig.4. Variation of nitrobenzene conversion with pressure (space velocity of nitrobenzene is 0.2 h^{-1} and temperature of 45°C)

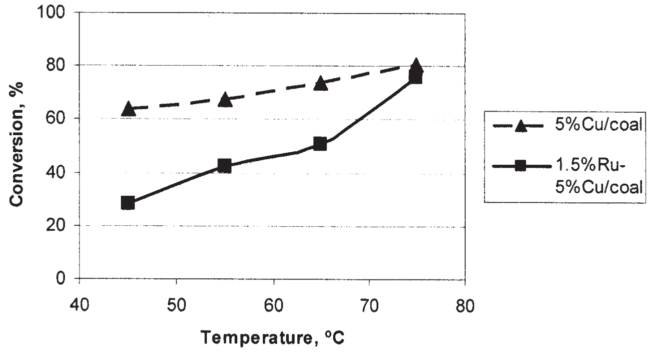


Fig. 5. Variation of nitrobenzene conversion with temperature (space velocity of nitrobenzene is 0.2 h^{-1} and of 25 atm pressure)

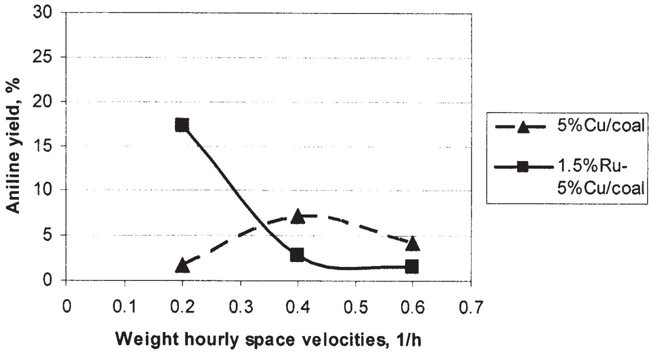


Fig. 6. Yield variation in aniline with weight hourly space velocity (40 atm pressure and 40°C temperature)

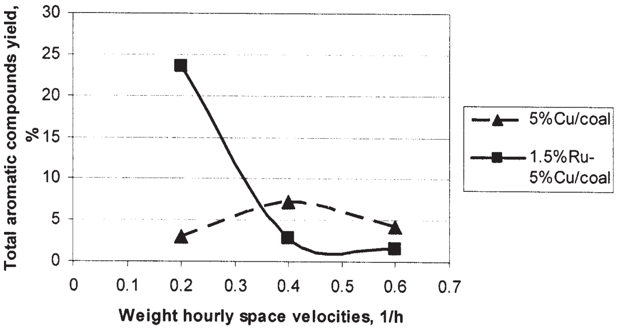


Fig. 7. Variation of yield in total aromatics derivatives, with weight hourly space velocity (40 atm pressure and 40°C temperature)

Variation of nitrobenzene conversion with temperature is shown in figure 5. Although the conversion of nitrobenzene has lower values at the catalyst 1.5% Ru-5% Cu /activated charcoal for the temperature range studied, the slope variation is greater for this catalyst than for the catalyst 5% Cu /activated charcoal.

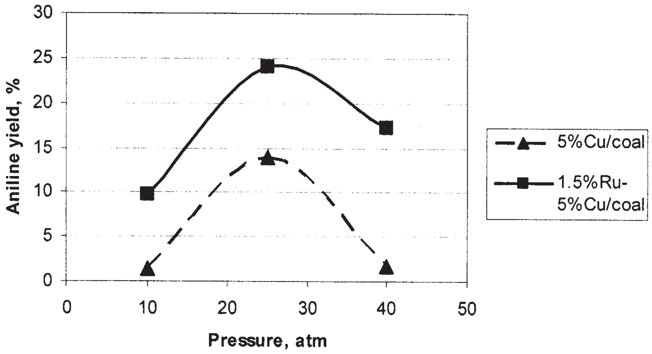


Fig.8. Variation of yield in aniline with pressure (space velocity of nitrobenzene is 0.2 h^{-1} and temperature of 45°C)

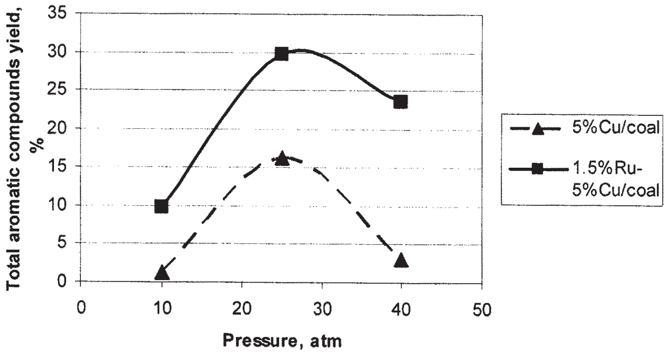


Fig. 9. Variation of yield in total aromatics derivatives with pressure (space velocity of nitrobenzene is 0.2 h^{-1} and temperature of 45°C)

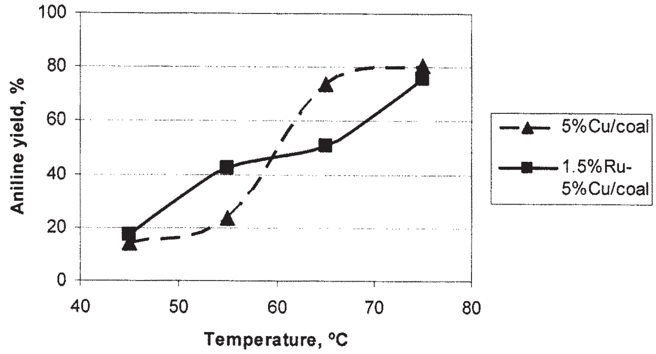
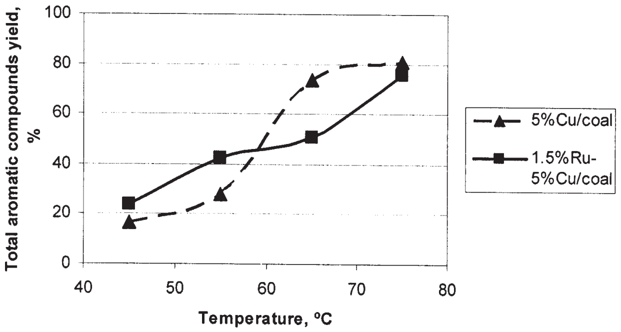


Fig. 10. Variation of yield in aniline with temperature (space velocity of nitrobenzene is 0.2 h^{-1} and pressure is 25 atm)

Yield in aniline and total aromatic derivatives on the catalyst 1.5% Ru-5% Cu / activated charcoal, shows a variation with weight hourly space velocity on a much larger range of values , than the catalyst 5% Cu /activated charcoal (figs. 6 and 7). Lower values of yield in aniline and total aromatic derivatives, at higher contact time, is probably due to the competing reaction of hydrogenation of the aromatic ring which is favored at these values of contact time.

Variation of yield in aniline and in total aromatics derivatives with pressure is shown in figures 8 and 9. For both catalysts is observed a similar variation with the variation of the conversion of nitrobenzene. Thus the variation curve of yield in aniline and total aromatics derivatives with the pressure shows a maximum variation for both catalysts. Like in the variation of nitrobenzene conversion with pressure, the decrease of yield in aniline and in total aromatics derivatives, with the increase pressure to values higher than 25 atm, is probably due to the same cause, namely the decrease of catalyst activity as a consequence of sintering catalyst when the



Fig, 11. Variation of yield in total aromatics derivatives with temperature (space velocity of nitrobenzene is 0.2 h^{-1} and pressure is 25 atm)

hydrogenation of nitrobenzene to amines arising mainly in the liquid phase.

Variation of yield in aniline and in total aromatics derivatives with temperature is shown in figures 10 and 11. Increasing of yield in aniline and total aromatics derivatives shows values close for those two catalysts, the slope variation having higher values at higher temperatures for 1.5% Ru-5% Cu /activated charcoal catalyst.

Conclusions

Hydrogenation of nitrobenzene in n-heptane was performed on 1.5%Ru-5% Cu / granular activated charcoal catalyst and 5% Cu / granular activated charcoal catalyst, using a fixed bed catalytic reactor in continuous systems.

The reaction mixture was analyzed chromatography, and the major compounds identified at nitrobenzene hydrogenation were aniline, N-methyl aniline, diphenylamine, diphenylhydrazine, azobenzene and nitrocyclohexane.

Acid strength distribution of the two catalysts where determined by termodesorption of diethyl amine in the temperature range 20-700°C.

The variation of conversion with weight hourly space velocities is more pronounced in the case of the catalyst 1.5%Ru-5% Cu / activated charcoal.

The decrease of nitrobenzene conversion and aniline yield with the increase of the pressure at higher values than 25 atm, for both catalysts tested, probably is due to sintering of the catalyst which is favoured by high exothermicity the hydrogenation process of nitrobenzene to amines correlated with the increase in the proportion of nitrobenzene in liquid phase.

The catalyst 1.5% Ru-5% Cu /activated charcoal shows a variation of the nitrobenzene conversion and of the aniline yield with temperature, at a slope greater than for the catalyst 5% Cu / activated charcoal.

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