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CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

Investigating the Catalytic Hydrogenation of Nitrobenzene in Supercritical Carbon Dioxide Using Pd-Containing Catalysts

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Abstract—Results from investigating the catalytic hydrogenation of nitrobenzene using palladium catalysts in a $CO_{2(SC)}$ medium with a traditional solvent (isopropanol) and without a solvent are presented. The reaction conditions in the $CO_{2(SC)}$ are: temperature, 90°C; nitrobenzene mass, 2.4 g; mass of catalyst, 0.1 g; partial pressure of hydrogen, 5 MPs; partial pressure of carbon dioxide, 20 MPa. The process of nitrobenzene hydrogenation in the $CO_{2(SC)}$ is accelerated. The rate of formation of the target product (aniline) in the $CO_{2(SC)}$ medium is 3.5–5-fold higher than the reaction in isopropanol or without the solvent. The process selectivity is 92–95%.

Keywords: supercritical carbon dioxide, nitrobenzene, aniline, catalysis, reaction rate, hydrogenation
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INTRODUCTION

The catalytic hydrogenation of nitrobenzene is an important process in the chemical technology for the production of aniline, which is in turn used as an intermediate product for synthesis of polyurethanes, rubber, pharmaceutical preparations, pesticides, and herbicides [1]. Industrial nitrobenzene hydrogenation is conducted in both the gaseous and liquid phases. The process of gas-phase hydrogenation of nitrobenzene is usually conducted using Ni- or Cu-containing catalysts at partial hydrogen pressures of 0.1–0.5 MPa and temperatures of 250–300°C [2–5], while liquid-phase hydrogenation with the use of Pt-, Pd-, Ni-containing catalysts is conducted at temperatures of 50–100°C and pressures of 1–5 MPa, either in different solvents or without solvents [6–8]. The selectivity of target product formation is 75–95%.

The use of supercritical carbon dioxide ($CO_{2(SC)}$) in the selective hydrogenation of nitrobenzene has drawn considerable interest among researchers, due to the advantages provided by using $CO_{2(SC)}$ in organic synthesis: enhanced heat and mass transfer coefficients, the possibility of changing reaction paths related to the formation of new molecular complexes, ease of product separation from the solvent, and reduced fire hazard [1, 9, 10].

The results from our study of the catalytic hydrogenation of nitrobenzene to aniline in a ($CO_{2(SC)}$) medium using heterogeneous Pd-containing catalysts are presented below.

EXPERIMENTAL

Catalysts and Reagents

Catalysts 5% Pd/ACC and 5% Pd/Al_2O_3 (Sigma Aldrich); 5% Pd/Graphite (Johnsons Matthey); 2% Pd/AC, 0.5% Pd/Al_2O_3, and 0.5% Pd-Zn/Al_2O_3 (all three from the Redkino Catalyst Company) were purchased from their respective manufacturers and used without further modification. A 5 wt % Pd catalyst on activated carbon (5% Pd/AC) was produced by following the technique described below.

Our reagents were nitrobenzene pure for analysis (Merck Schuchardt OHG, S 6568270 308); carbon dioxide (GOST (State Standard) 8050–85), grade I; hydrogen (GOST (State Standard) 6709–72), grade I; nitrogen (GOST (State Standard) 9293–78), grade I; isopropanol, chemically pure (TU (Technical Specifications) 2632-009-0027787–02 ZAO Baza no. 1 Khimreaktivov); and pure sodium tetrachloropalladate (II) (TU (Technical Specifications) 2625-048-00205067–2003, OAO Aurat).

Synthesis of 5%Pd/AC Catalyst

The synthesis of 5 wt % Pd palladium on activated carbon was performed via impregnation according to the following scheme: a sample of activated carbon was pre-washed with water at room temperature and then dried under vacuum. A solution of precursor (sodium tetrachloropalladate) in a complex solvent with the composition methanol : tetrahydrofuran : water at a

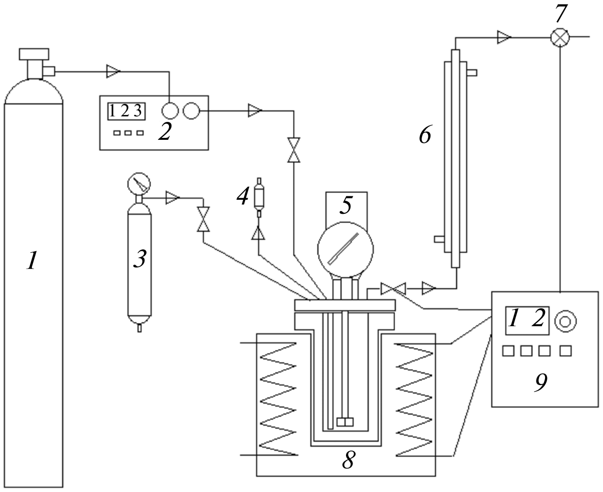

Fig. 1. Setup for the catalytic hydrogenation of nitrobenzene in the supercritical CO_2 medium: (*1*) cylinder with carbon dioxide; (*2*) positive displacement pump; (*3*) gas burette; (*4*) sampling outlet; (*5*) autoclave; (*6*) reflux condenser; (*7*) valve; (*8*) heater; (*9*) temperature and mixing rate controller.

volume ratio of 5 : 1 : 1 was added to an aliquot of dried activated carbon AU-100. The catalyst was dried under vacuum following sorption.

Preliminary reduction of catalysts was performed in a hydrogen flow at 300°C over 4 h.

Nitrobenzene Hydrogenation

Nitrobenzene hydrogenation was conducted in the setup shown in Fig. 1. A Parr Instruments 4307 high-pressure reactor (United States) with total flask volume of 100 cm^3 and a maximum operating pressure of 100 MPa was used as autoclave *5*. Carbon dioxide was pumped with a Supercritical 24 positive displacement pump (United States).

A four-blade rotor mixer powered by an electric motor at a maximum 700 revolutions per minute was used for mixing the reaction medium. Pressure was controlled with a manometer. The thermostating of the reactor was controlled using heating block *8* with programmable controller *9*. Temperature was maintained with an accuracy of 0.1°C.

The standard experiment was conducted as follows: A flask with aliquots of catalyst and nitrobenzene was purged three times with 300 ml of carbon dioxide at a pressure of 2 MPa, followed by heating of the mixture to the required temperature. Carbon dioxide was then delivered by a pump up to the indicated pressure (1–20 MPa). When $CO_{2(SC)}$ equilibrium was reached, gaseous hydrogen was fed into the reactor through a burette. It was at this point that the reaction time began.

Analysis of Reaction Mixture

Qualitative identification of intermediates in the synthesis was conducted using gas-liquid chromatography with mass-spectral detection of compounds. A GS-2010 gas chromatograph (Shimadzu, Japan) equipped with an HP-1MS 30 m × 0.25 mm × 0.25 μm capillary column with an efficiency of 4300 theoretical plates for pentadecan and a single GSMS-QP2010S quadruple gas mass spectrometer (Shimadzu, Japan) were used. Our reaction mixture analysis was conducted in the thermoprogrammed mode with an initial column temperature of 80°C (5 min), a linear temperature rise from 80 to 150°C at a rate of 10 degree/min, and exposure at 150°C for 10 min. Helium (extra pure grade 6.0) was used as a carrier gas. The helium pressure was 63 kPa; the flow rate, 20 mL/min; the linear rate of the gas carrier in the column, 36 cm/min; the injector temperature, 300°C; the interface temperature, 280°C; and the ion source temperature, 260°C.

Quantitative analysis of the reaction mixture was performed via high performance liquid chromatography using an Ultimate 3000 chromatographic system equipped with a Spectroflow 757 spectrophotometric detector operating at a wavelength of 254 nm. The system was also equipped with a peristaltic pump with automated washing of the working pump pistols, a system of solvent purification, a needle port, and an analytical stainless steel column 150 × 2 mm in size. A Reprosil ODS-A C-18 polymeric support was used as the stationary phase. The column efficiency was 15000 theoretical plates; the coefficients of peak asymmetry did not exceed 1.005. Water and acetonitrile acidified with trifluoroacetic acid were used as the mobile phase. The elution rate was 0.5 mL/min; the pressure at the column inlet was 2.4 MPa. Chromatographic analysis was performed at 30°C. Concentrations of nitrobenzene and aniline were determined using standard compounds and their respective calibration dependences with toluene as an external standard.

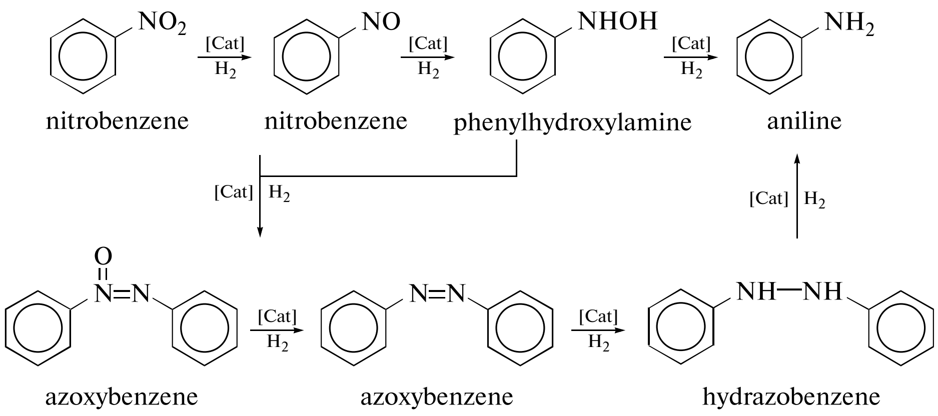

Fig. 2. Scheme of nitrobenzene catalytic hydrogenation in the presence of Pd-containing heterogeneous catalyst.

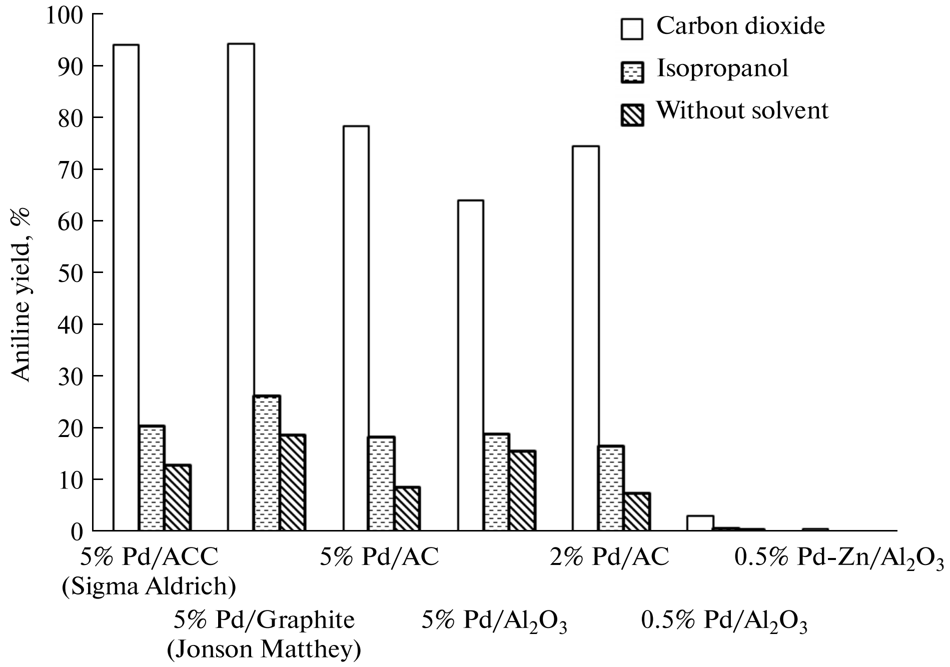

Fig. 3. Screening of the activity of hydrogenation catalysts in a $CO_{2(SC)}$ medium, in isopropanol, and without solvent. Conditions: $T = 90°C$; $P_{H_2} = 5$ MPa; $P_{CO_2} = 20$ MPa; nitrobenzene mass, 2.4 g; catalyst mass, 0.1 g; isopropanol volume, 100 cm^3; substrate/catalyst = 24/1; reaction time,180 min.

RESULTS AND DISCUSSION

The initial substrate (nitrobenzene), major product (aniline), and intermediate reaction products (nitrosobenezene, phenylhydroxylamine, azoxybenzene, azobenzene, and hydrazobenzene) were found by analyzing the mixture of the hydrogenation reaction conducted in $CO_{2(SC)}$ or isopropanol. Based on this data, we propose the scheme for the catalytic nitrobenzene hydrogenation process presented in Fig. 2.

Nitrobenzene hydrogenation in the $CO_{2(SC)}$ medium was conducted under the following conditions: temperature 90°C; nitrobenzene mass 2.4 g; catalyst mass (5% Pd/ACC, 5% Pd/Graphite, 5% Pd/Al_2O_3, 2% Pd/AC, 0,5% Pd/Al_2O_3, 0.5% Pd-Zn/Al_2O_3, 5% Pd/AC) 0.1 g; hydrogen partial pressure $P_{H_2} = 5$ MPa; and carbon dioxide partial pressure $P_{CO_2} = 20$ MPa. When the nitrobenzene hydrogenation reaction was conducted in the isopropanol medium, the volume of the latter was 100 cm^3, and carbon dioxide was replaced with extra pure nitrogen at an equal partial pressure of 20 MPa in order to ensure identical process conditions. The reaction time was 180 min.

The data presented in Fig. 3 indicate that the formation rate of the target product (aniline) in the

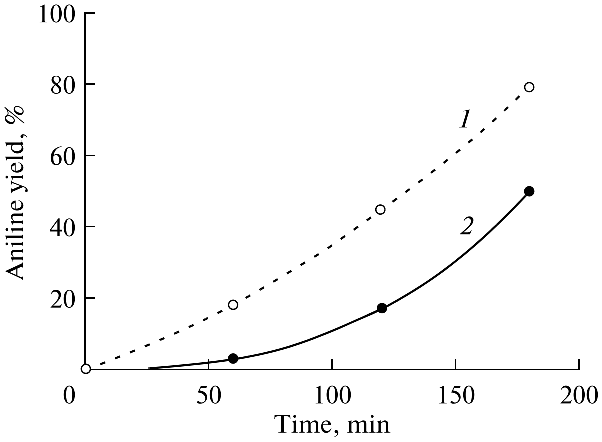

Fig. 4. Aniline yield in the reaction of nitrobenzene hydrogenation on (*1*) reduced and (*2*) non-reduced samples of 5% Pd/AC catalysts. Conditions: $T = 90°C$; $P_{H_2} = 5$ MPa; $P_{CO_2} = 20$ MPa; nitrobenzene mass, 2.4 g; catalyst mass, 0.1 g; substrate/catalyst = 24/1.

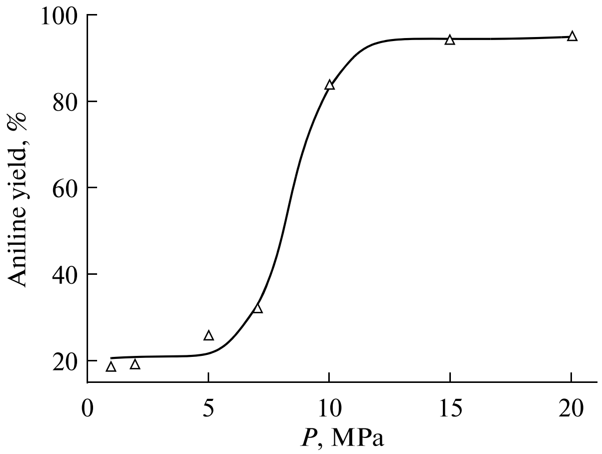

Fig. 5. Effect of carbon dioxide pressure on the aniline yield in the reaction of nitrobenzene hydrogenation on 5% Pd/AC catalyst. Conditions: $T = 90°C$; $P_{H_2} = 5$ MPa; nitrobenzene mass, 2.4 g; catalyst mass, 0.1 g; isopropanol volume, 100 cm^3; substrate/catalyst = 24/1; reaction time, 180 min.

$CO_{2(SC)}$ medium was 3.5 to 5 times higher than for the reaction in isopropanol or without the use of solvent.

Among the investigated catalysts, the 5% Pd/Graphite (Johnson Matthey) sample displayed the highest activity in nitrobenzene hydrogenation in both the $CO_{2(SC)}$ medium and the common solvents. The activity of the investigated catalysts fell by more than 20 times as the active metal content was reduced from 5 to 0.5 wt %. The selectivity of the hydrogenation of nitrobenzene into aniline in the $CO_{2(SC)}$ medium was 92–95% for all of the investigated catalysts. The catalyst samples with 5% palladium content (5% Pd/ACC (Sigma Aldrich) and 5% Pd/Graphite (Johnsons Matthey) displayed the best results in this reaction. In addition, the effect of the support (activated carbon for 5% Pd/ACC and graphite for 5% Pd/Graphite) was almost entirely eliminated in the $CO_{2(SC)}$ medium. At the same time, the 5% Pd/Graphite (Johnsons Matthey) catalyst was found to be more active when the reaction was conducted in isopropanol or without the solvent, due possibly to the better accessibility of catalytic centers of metallic palladium on the graphite surface, relative to the palladium active centers in the activated carbon matrix.

The effect of prereduction on the process of nitrobenzene hydrogenation in the $CO_{2(SC)}$ medium was investigated for the synthesized 5% Pd/AC catalyst. The experiments were performed under the conditions described above with both prereduced and non-reduced samples of the 5% Pd/AC. It was found that the prereduction of the catalyst doubled the rate of aniline formation, compared to the non-reduced catalyst (Fig. 4). A long induction period related to the reduction of palladium (II) chloride complex in the process of nitrobenzene hydrogenation was observed in the case of non-reduced catalyst. It was the reduced palladium that ensured the higher reaction rate.

Our experiments with the most active catalyst 5% Pd/Graphite (Johnsons Matthey) under the conditions described above were performed by varying the carbon dioxide partial pressure in order to determine the effect the carbon dioxide pressure had on the process of nitrobenzene hydrogenation (Fig. 5). It can be seen that the raising the carbon dioxide partial pressure from 1 to 7 MPa resulted in a gradual increase in the aniline yield, from 18 to 32%. Raising the partial pressure to 12–13 MPa resulted in a jump-like increase of the aniline yield to 90–94%, due to a considerable reduction in diffusional limitations. The higher carbon dioxide pressure did not affect the aniline yield.

CONCLUSIONS

Supercritical carbon dioxide ($CO_{2(SC)}$) is a promising solvent for conducting organic synthesis, including the hydrogenation of nitro derivatives. The effectiveness of its use was demonstrated via the example of catalytic nitrobenzene hydrogenation using traditional Pd-containing catalysts. The rate of formation for the target product (aniline) in a $CO_{2(SC)}$ medium was 3.5 to 5 times higher than with the reaction conducted in isopropanol. The selectivity of the process was 92–95%.

The effect the support had on the activity of heterogeneous catalysts diminished in the $CO_{2(SC)}$ medium, indicating enhanced accessibility of the active Pd-centers for the reactant.

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