

PHYSICAL CHEMISTRY OF HYBRID NANOMATERIALS
AND MULTICOMPONENT SYSTEMS

Highly Efficient Pt-Catalyst Supported on Mesoporous Ceria-Zirconia Oxide for Hydrogenation of Nitroaromatic Compounds to Anilines¹

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Abstract—In this work, we have prepared a new catalytic system based on highly dispersed Pt nanoparticles supported on mesoporous ceria-zirconia oxide. The unique ability of the synthesized catalyst to activate hydrogen in the temperature range from -50 to 25°C allows us to provide selective hydrogenation of nitroaromatic compounds to anilines at room temperature and atmospheric pressure of H_2 .

Keywords: anilines, amines, Pt nanoparticles, hydrogenation, mesoporous ceria-zirconia oxide

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Hydrogenation of nitroaromatics to the corresponding anilines is the simplest way to obtain this important class of organic compounds, which are actively used in synthesis of pharmaceuticals, dyes and plastics [1]. For the synthetic purposes, the reduction of nitroaromatics is usually performed with the use of metallic Zn in an excess of HCl. This method requires additional stages of product purification, removing the excess of reagents, and, in addition, the process is not scalable. According to the modern organic synthesis concept that implies the principles of “green chemistry,” heterogeneous hydrogenation is the most perspective methodology to obtain anilines from nitroaromatics [2]. The heterogeneous systems based on non-noble metals like Co, Ni, Ag [3, 4] and supported Pt, Pd, Au nanoparticles are now used as hydrogenation catalysts [5–7]. Furthermore, the catalysts containing non-noble metals show a much lower activity compared to the systems with noble metals [8].

The ability of Pt nanoparticles to activate hydrogen has attracted the attention to the synthesis of hydrogenation catalysts with this active metal. Among the proposed systems, Pt nanoparticles supported on reducible oxide systems are of high interest. Thus, by using a Pt/ FeO_x catalyst, it was possible to obtain a wide range of anilines with yields up to 90%, yet the reaction was performed under H_2 pressure (3 bar) and temperature 40°C [9]. Corma et al. [10] used a Pt/ TiO_2 catalyst for hydrogenation of substituted nitroaromat-

ics at temperatures of 30 – 60°C under 3–6 bar of H_2 . The Pt nanoparticles deposited on the MFI zeolite also showed activity in the selective hydrogenation of nitroaromatic compounds, but a long reaction time (8–10 h) was required to achieve high yields, as well as rather stringent process conditions: 80°C , hydrogen pressure 10 bar [11].

To increase the selectivity of hydrogenation of nitroaromatic compounds to anilines, in particular, containing other reducible groups, and also for the simplicity of the process, it becomes promising to create a catalytic system that provides high yields of anilines of different structures under normal conditions: at atmospheric pressure and room temperature. In this paper, we propose a new catalytic system based on supported Pt nanoparticles on a mesoporous cerium-zirconium oxide as a carrier. As shown in [12], oxygen vacancies of cerium oxide are the centers of adsorption and activation of the nitro group. The number of these centers can be increased by doping cerium oxide with zirconium cations, which facilitates the redox cycle of CeO_2 and the formation of a number of Ce^{3+} centers [13, 14]. The deposition of Pt nanoparticles on a CeO_2 – ZrO_2 substrate also promotes an additional reduction of Ce^{4+} to Ce^{3+} , with Pt being the center of hydrogen activation. Another important factor of the high activity of the catalyst is its developed surface, which in the present work is achieved by creating a mesoporous oxide support structure.

¹ The article was translated by the authors.

EXPERIMENTAL

Support Synthesis

The preparation of mixed oxide substrates CeO₂–ZrO₂ was carried out by a coprecipitation method [15]. The precursor for the zirconium solution was ZrO(NO₃)₂ · xH₂O (99.5%; Acros Organics) and (NH₄)₂Ce(NO₃)₆ (98+%, Alfa Aesar) was used as a precursor for the cerium containing solution. For the synthesis of cerium-zirconium supports with the molar ratio Ce : Zr = 0.8 : 0.2, simultaneous co-precipitation of cerium and zirconium hydroxides from working solutions in the presence of ammonium hydroxide was performed.

A solution containing 0.73 mol of the cerium precursor was prepared by dissolving the sample in water and then diluted with isopropanol (99%) in a 1.7 : 1 ratio. After dilution, the resulting solution was stirred at room temperature for 1 h.

To obtain a solution containing 0.19 mol of the zirconium precursor, the sample was dissolved in a 2.3 M solution of oxalic acid. The resulting solution was diluted with isopropanol (99%) in a 1 : 1 (v/v) ratio. After dilution, the solution was stirred at room temperature for 1 hour. To co-precipitate cerium and zirconium hydroxides, the working solutions were poured off under vigorous stirring and an ammonia solution (23 wt %) was added until pH reached 9.15. The resulting suspension was stirred for 30 min, after which the precipitate was separated, washed with deionized H₂O and dried for 12 h at 70°C, followed by calcination at 400°C in a closed crucible for 4 h.

Catalyst Synthesis

Synthesis of a catalyst with a platinum content of 1 wt % was performed by the method of pH-controlled precipitation of the precursor. An aqueous solution of H₂PtCl₆ (50 mL) with a concentration of 0.46 mM was prepared, after that an aqua solution of Na₂CO₃ (0.1 M) was added until pH 7. Then, a sample of CeO₂–ZrO₂ was added and the suspension was stirred for 30 min without heating and then the suspension was stirred for 3 h at 60°C. The completeness of Pt deposition was checked by the qualitative reaction of Ptⁿ⁺ ions in the parent solution with KI and HCl. In all cases, we observed a complete Pt deposition onto the support surface. The precipitate was then separated and washed with deionized H₂O, dried under vacuum using a rotary evaporator until complete removal of moisture. The resulting catalyst was reduced in a flow of hydrogen at 250°C for 2 h. The catalyst was designated as 1Pt/CZ-N.

Physicochemical Characterization

Transmission electron microscopy (TEM). A target-oriented approach was utilized for the optimization of

the analytic measurements [16–18]. Before measurements, the samples were mounted on a 3 mm copper grid and fixed in a grid holder. The samples morphology was studied using a Hitachi HT7700 transmission electron microscope. Images were acquired in a bright-field TEM mode at a 100 kV accelerating voltage.

Energy-dispersive X-ray spectroscopy (EDS-SEM). The samples morphology was studied under native conditions to exclude metal coating surface effects. The observations were carried out using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in a secondary electron mode at a 10, 15, and 20 kV accelerating voltage and at a working distance 15 mm. EDX studies were carried out using an Oxford Instruments X-max EDX system.

X-ray diffraction analysis (XRD). The phase composition of the samples and the size of the primary crystals of crystalline phases were determined by the XRD method. X-ray diffraction patterns were recorded on a DRON-2 device in Ni-filtered CuK_α radiation ($\lambda = 0.1542$ nm) in a step-scan mode (in 0.02° increments) in the range $2\theta = 10^\circ$ – 80° . The identification of the phase composition was carried out by matching the position and intensity of the lines on the X-ray diffraction pattern with the ICDD data (International Data Center for X-ray Diffraction). The coherent scattering domain size was calculated from the broadening of the X-ray diffraction lines in accordance with the Scherer equation.

Temperature-programmed reduction with hydrogen (TPR-H₂). TPR measurements were carried out on a laboratory constructed flow-system equipped with a gas purification system, a quartz U-shaped reactor, a water vapor trap, and a thermal conductivity detector. The detector was calibrated by reduction of a CuO sample (Aldrich-Chemie GmbH, 99%) treated in an Ar flow at 300°C. All experiments were conducted with a water vapor trap, which was cooled to –100°C. A sample of 1% Pt/CZ-N with a weight of 150 mg was treated in an Ar flow at 250°C for 90 min. The catalyst was then cooled to –50°C using a mixture of ethanol and liquid nitrogen as a cooling mixture and thermostatted at this temperature for 60–90 min. Heating from –50 to 25°C was carried out in a flow of a gas mixture of 4.6% H₂/Ar (30 mL/min) at a heating rate of 10 deg/min. The sample was kept at room temperature (25°C) until the uptake of hydrogen ceased.

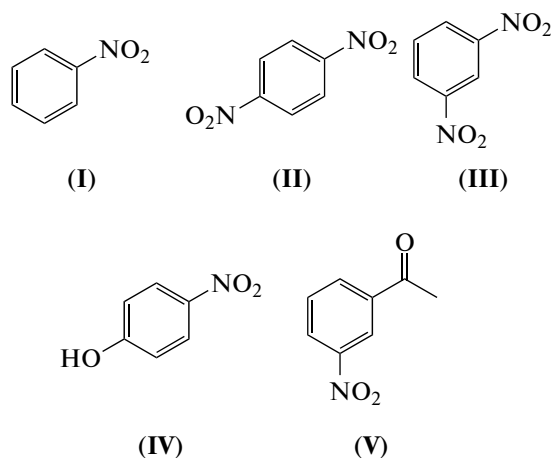
Specific surface area and porosity. N₂ adsorption-desorption isotherms were obtained on an ASAP 2020 Plus “Micromeritics” sorptometer at 77 K. The BET method was used to calculate the specific surface area (S_{BET}) of the sample. The total pore volume (V) was

calculated at $p/p_0 = 0.99$. The t -plot method was used to control the volume of micropores. The pore size distribution (PSD) was calculated from the isotherm desorption branch by the BJH method.

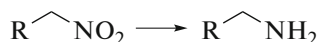
Dispersion of Pt nanoparticles. The metal dispersion was determined by irreversible chemisorption of CO at 35°C on ASAP 2020 Plus Micromeritics. The samples of the reduced catalysts before the measurement of chemisorption were additionally reduced in the ASAP unit with hydrogen at a temperature of 250°C for 30 min in a flow of pure H₂ (300 mL/min).

Catalytic Experiment

In this work, the following of nitroaromatic compounds were used:



The liquid-phase hydrogenation reaction of nitroaromatic compounds can be presented as:



It was carried out at room temperature under an atmospheric pressure of H₂. A sample of the catalyst (50 mg) was placed in a round-bottomed three-necked flask and the system was purged with hydrogen for 30 min. A solution of the substrate in ethanol 0.2 M (or in tetrahydrofuran in the case of using *o*- and *p*-dinitrobenzene as a substrate) was then poured into the reactor by means of a feed cock of the reaction mixture. The concentration of platinum in the reaction mixture was 0.85 mol %. The reaction was carried out with vigorous stirring on a magnetic stirrer at a rate of 900 rpm in the monitoring mode by means of gas-liquid chromatography until the peak of the starting compound disappeared on the chromatogram. At the end of the experiment, the stirring was stopped; the catalyst was separated from the reaction mixture by centrifugation.

Analysis of the reaction products was performed using GC with a Chromatek Crystal 5000.2 chromatograph with a flame ionization detector (FID) and a capillary column CR-5 (2 mm × 25 m) at a temperature of 190°C. The peaks were identified on the basis

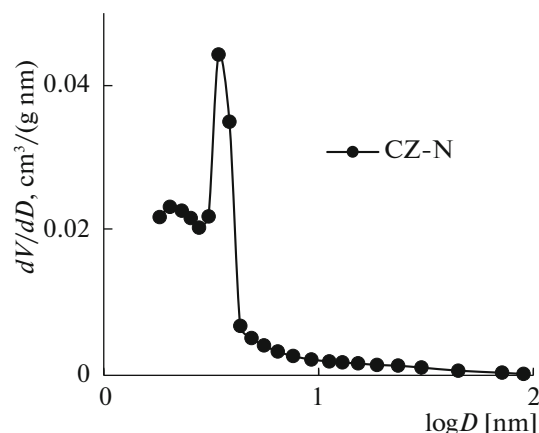


Fig. 1. The pore size distribution of the support CeO₂-ZrO₂, D is pore diameter.

of the experimentally obtained retention times of individual compounds (nitrobenzene, *o*-dinitrobenzene, *p*-dinitrobenzene, *p*-hydroxynitrobenzene, *p*-nitroacetophenone, nitrocyclohexane, aniline, *o*-phenylenediamine, *p*-phenylenediamine, *p*-hydroxyaniline, *p*-nitrophenylethanol, aminocyclohexane). The structure and purity of the products obtained were confirmed by NMR spectroscopy. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer in solvents CDCl₃ and DMSO-d₆.

RESULTS AND DISCUSSIONS

The method used for the synthesis of the oxide carrier CeO₂-ZrO₂ made it possible to obtain a mixed oxide with the CeO₂ cubic fluorite structure ($a = 5.41 \text{ \AA}$) with a coherent scattering domain size of 5 nm, with ZrO₂ being the X-ray amorphous phase. It should be noted that the surface area of the obtained mixed oxide is as high as 104 m²/g; the sample has a mesoporous structure with a narrow pore size distribution and an average diameter of 3 nm (Fig. 1). The microstructure of the sample is shown in Fig. 2a.

The deposition of Pt nanoparticles (NPs) on the mixed oxide made it possible to obtain nanoparticles with an average size of 4 nm according to the TEM data (Fig. 2b). However, according to the CO adsorption data, the dispersion of the deposited metal exceeds 50%, and the average size of the Pt nanoparticles is 2 nm.

The SEM-EDX micrographs of the obtained 1% Pt/CZ-N catalyst confirmed a uniform distribution of CeO₂ and ZrO₂ in the sample, as well as Pt NPs on the surface of the mixed-oxide support (Fig. 3). The study of the reduced catalyst sample of 1% Pt/CZ-N by the TPR-H₂ method showed an

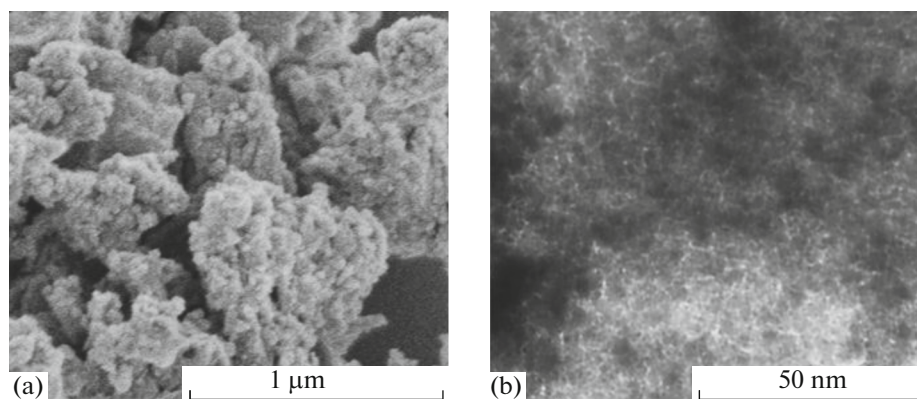


Fig. 2. Micrographs of the prepared samples: (a) the SEM image of the CZ-N support, (b) the TEM image of the 1% Pt/CZ-N catalyst.

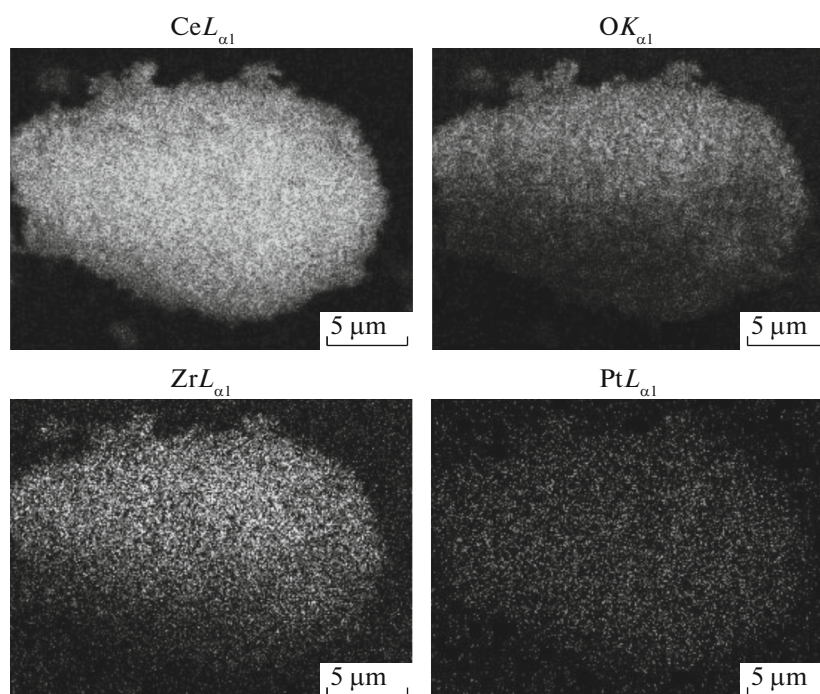


Fig. 3. The SEM-EDX images of the 1% Pt/CZ-N catalyst.

anomalously high hydrogen uptake in the temperature range from -50 to 25°C (Fig. 4); the molar ratio of H_2 : Pt exceeded the stoichiometric one by 11 times.

The intensive hydrogen absorption at low temperatures on the catalytic system under study can be explained by the appearance of the hydrogen spillover effect, and, consequently, H_2 activation in the investigated temperature region leading to a partial reduction of the carrier and the formation of Ce^{3+} centers on which the nitro group can be adsorbed [12]. The resulting “active” hydrogen is capable of hydrogenating the nitro group under normal conditions: at room temperature and atmospheric pressure.

The catalytic system used allows the production of amines with quantitative yields. Complete hydrogenation of nitrobenzene proceeded within 2 h. Hydrogenation of *m*- and *p*-dinitrobenzene resulted in diamines with a quantitative yield in 3 h. When hydrogenating *p*-nitrophenol, the mild reaction conditions did not affect the substituent in the benzene ring and produce the corresponding *p*-aminophenol in 2 h. By varying the reaction time, it is possible to obtain both the corresponding *m*-aminoacetophenone (in 2 h) and 1-(3-aminophenyl)ethanol (in 5 h) from *m*-nitroacetophenone.

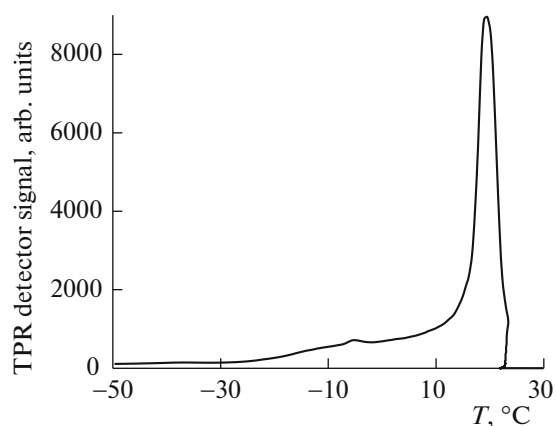


Fig. 4. TPR- H_2 profile of the reduced 1% Pt/CZ-N catalyst.

For comparison, in [19] the use of a stoichiometric reductant, hydrazine hydrate, allowed to reach the quantitative yield of 4-hydroxyaniline only at 100°C in 5 h. In the other work [20], it was reported on the hydrogenation of nitrobenzene on a homogeneous catalyst $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ ($\omega(\text{Pd}) = 2.5\%$): the yield of aniline at room temperature in 3 h was 76%.

Thus, the synthesized catalyst with a 1% platinum content supported on the mesoporous cerium-zirconium oxide exhibited a high catalytic activity in the hydrogenation of various nitroaromatic compounds to anilines at an atmospheric pressure and room temperature. The unusual activity of the 1% Pt/CZ-N catalyst is associated with the hydrogen spillover effect observed even at sub-ambient temperatures, which results in the formation of active hydrogen and a partial reduction of the cerium-zirconium carrier with the formation of adsorption and activation sites for the substrate.

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