

Nanocolloidal Ru/MgF₂ catalyst for hydrogenation of chloronitrobenzene and toluene

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The use of magnesium fluoride support for ruthenium active phase allowed obtaining new catalysts of high activities in the hydrogenation of toluene and ortho-chloronitrobenzene. Ruthenium colloid catalysts (1 wt.% of Ru) were prepared by impregnation of the support with the earlier produced polyvinylpyrrolidone (PVP)-stabilized ruthenium colloids. The performances of the colloidal catalysts and those obtained by traditional impregnation were tested in the reactions of toluene hydrogenation to methylcyclohexane and selective hydrogenation of ortho-chloronitrobenzene (o-CNB) to ortho-chloroaniline (o-CAN). It was shown that the use of chemical reduction method allows obtaining highly monodisperse ruthenium nanoparticles of 1.6–2.6 nm in size. After reduction in hydrogen at 400°C, the colloidal ruthenium nanoparticles were found to strongly interact with MgF₂ surface (SMSI), which decreased the catalyst ability to hydrogen chemisorption, but despite this, the colloid catalysts showed higher activity in o-CNB hydrogenation and higher selectivity to o-CAN than the traditional ones. It is supposed that their higher activity can be a result of high dispersion of Ru in colloid catalysts and the higher selectivity can be a consequence of the lower availability of hydrogen on the surface.

Keywords: ruthenium nanocolloidal catalyst, magnesium fluoride, toluene hydrogenation, reduction of chloronitrobenzene.

INTRODUCTION

Metal nanoparticles on a properly chosen support make an interesting alternative to conventional catalysts prepared by the impregnation method. Similarly as for conventional catalysts, the interactions of metal nanoparticles with the support surface affect their catalytic properties. One of supports that strongly modifies the properties of active phase placed on its surface is magnesium fluoride. It was found to be an interesting support of catalysts for hydrodesulphurisation^{1, 2}, hydrodechlorination^{3, 4}, NO reduction in the presence of hydrocarbons as reducing agents^{5–7}, CO oxidation⁸, hydrogenation of benzene^{9, 10} and toluene^{11–13} and recently also for chloronitrobenzene hydrogenation to chloroaniline^{14, 15}. A great advantage of magnesium fluoride is its easy preparation and availability as well as the low price of reactants used for its synthesis. Magnesium fluoride is a good mesoporous support having well-developed porous structure, high chemical inertness, thermal stability and hardness^{16, 17}.

Selective catalytic reduction of halogenated nitroaromatic compounds is the most widely used method for the syntheses of halogenated anilines – important reagents for the manufacture of a wide variety of drugs, pesticides, pigments and dyes. The highest catalytic activity in this reaction show platinum group metals. The reduction of nitro group in nitrobenzene proceeds without major difficulties. However, the nitro group, in halogen-containing nitroaromatics, is accompanied by a halogen substituent which easily undergoes hydrogenolysis in the reaction conditions. Therefore, the search is continued for catalysts of the highest possible hydrogenation activity and the lowest possible hydrodehalogenation activity. One direction in the search for better catalyst is the modification of the properties of the commonly used metals by supporting them on unconventional supports such as ZrO₂¹⁸, g-ZrP, SnO₂¹⁹, g-Fe₂O₃^{20, 21}, and carbon nanotubes²² as well as modification of the active metal.

The practical importance of chloronitrobenzene hydrogenation results from a large variety of applications of products of the above reaction – chloroanilines. For example *o*-chloroaniline is used as an intermediate in the production of a number of products, including agricultural chemicals, azo dyes and pigments and pharmaceuticals, it is also used in petroleum solvents and fungicides and as a cross linking agent for polyurethane resins. One of the compounds produced on the basis of *o*-chloroaniline is salicylidene-2-chloroaniline – the compound showing photochromism²³. Such compounds are employed as components of molecular switches for data storage, for the production of colour changing lenses for sunglasses. One of the most popular diuretics – *Chlorothiazide*, is produced on the basis of *m*-chloroaniline²⁴. A widely applied chloronitrobenzene isomer is its *para* isomer applied to the manufacture herbicides and insecticides such as *Monolinuron* and *Monuron*, as well as pharmaceuticals and cosmetics. It is also needed for the production of *Triclorocarban* that is applied as an antiseptic and deodorizing agent. A popular disinfectant is *Chlorhexidine*²⁵ which is a component of oral cavity disinfecting agents. Other examples of the application of chloroanilines are presented in²⁶.

Benzene, toluene, and xylene are all aromatic compounds important for the production of polymers, other chemicals, and numerous consumer products (solvents, paints, polishes, pharmaceuticals). In industry, products of hydrogenation of aromatic hydrocarbons are the starting materials for large-volume syntheses. The product of benzene hydrogenation, cyclohexane, is a raw material for the production of caprolactam (a substrate for obtaining nylon) and adipic acid (a substrate for the manufacture of saturated polyesters and plasticizers for plastics). About 80–85% of the annual production of cyclohexane is used for the manufacture of nylon 6 and nylon 6.6 and originates just from catalytic hydrogenation of benzene²⁷. Taking into regard that turnover

the frequencies and reaction probabilities decrease in the order benzene>toluene>o-xylene²⁸, and the well-known carcinogenic properties of benzene, toluene hydrogenation was chosen as the test reaction. The most frequently used active phases for hydrogenation catalysts are platinum group metals – platinum²⁹, palladium³⁰ and ruthenium³¹, of which ruthenium is the cheapest³².

In the present study we have employed MgF₂ as a support for ruthenium colloidal particles of high monodispersity. To the best of our knowledge this is the first report on the potential application of colloidal Ru/MgF₂ system as the hydrogenation catalyst. The use of colloidal particles was aimed at unifying the catalytic properties of the metallic particles by unification of their size.

EXPERIMENTAL

Preparation of supports and catalysts

Magnesium fluoride was obtained by adding small portions of MgCO₃ × 2H₂O to an aqueous solution of hydrofluoric acid until neutralisation followed by acidification with a few additional drops of the acid. The precipitate was then aged at room temperature for a few days under stirring, dried at 80°C and calcined at 400°C for 4 h. After the calcination, MgF₂ was ground to obtain particles of 0.2–0.5 mm in size.

Synthesis of PVP-stabilised ruthenium nanoparticles

A ruthenium colloid was prepared by the reduction of RuCl₃ × 3H₂O with methanol in the presence of poly-N-vinyl-2-pyrrolidone (average mol wt = 19 000). The method for the preparation of ruthenium colloids was adapted from³³. By applying three different concentrations of ruthenium(III) chloride (1, 3 and 5 mmol/dm³) three PVP-stabilised ruthenium colloids (R1, R3, R5) were obtained. Mole ratio of PVP/Ru was 20:1 in each case (Table 1). The preparation consisted in dropping a solution containing methanol (reducing agent) and 0.2M NaOH (reaction initiator) into a solution containing RuCl₃ × 3H₂O, water and PVP. The reaction was carried out at 60°C for 3 h.

Synthesis of ruthenium nanoparticles catalysts and Ru/MgF₂ catalyst

The ruthenium colloid prepared in the above way were supported on magnesium fluoride by impregnation method. The obtained samples were denoted as R1/F, R3/F, R5/F. Before being tested in the reaction, they were reduced in hydrogen flow at 400°C for 2 h. All the catalysts contained 1 wt.% Ru.

The “Ru/MgF₂ conventional” catalyst was prepared by conventional impregnation using an aqueous solution of RuCl₃ × 3H₂O. The required amount of RuCl₃ × 3H₂O was dissolved in water, then contacted with MgF₂ at room temperature for several minutes, followed by evaporation of water. The solid was dried at 80°C, then reduced at 400°C under hydrogen flow (100 cm³ × min) for 4 h. The Ru content was 1 wt.%.

Catalyst characterisation

TEM studied

The JEOL 2000 instrument with 80kV electron beam was used for TEM studies. Methanol suspension of ruthenium colloids was prepared by means of ultrasonic waves and then the suspension was supported as a thin film on the holey carbon.

The determination of metal dispersion by hydrogen chemisorption

All chemisorption experiments were performed on an ASAP 2010C sorptometer. Hydrogen chemisorption measurements were carried out at 100°C.

Prior to hydrogen chemisorption, the samples were pretreated in situ to remove the adsorbed molecules from the surface of ruthenium. The samples were evacuated for 15 min at room temperature and next at 400°C for 60 min, followed by reduction in hydrogen flow (40 cm³ × min⁻¹) at 400°C and evacuated again for 120 min at 400°C.

The dispersion (*D*) and metallic surface area (*S*) was calculated using the following equation³⁴:

$$S = \frac{v_m \cdot N_A \cdot n \cdot a_m \cdot 100}{22414 \cdot m \cdot wt} (m^2 g_{Ru}^{-1})$$

where *v_m* is H₂ adsorbed volume expressed in cm³, *N_A* is Avogadro's number (6.022 × 10²³ mol⁻¹), *n* is the chemisorption stoichiometry (= 2), *a_m* is the surface area (m²) occupied by a metal atom, *m* is the sample mass (g), *wt* (%) is the metal loading.

The dispersion of active phase can be calculated from the formula:

$$D = \frac{S \cdot M}{a_m \cdot N_A}$$

where *S* is the metallic surface area, *M* is molar mass of ruthenium (101.07 g × mol⁻¹), *N_A* is Avogadro's number and *a_m* is the surface covered by one ruthenium atom.

Catalytic test – hydrogenation of chloronitrobenzene

Hydrogenation reaction was carried out for 2h under hydrogen pressure of 4.0 MPa in a 200 cm³ stainless steel autoclave with a glass tube inside, equipped with a magnetic stirrer. The autoclave was loaded with 0.05 g of catalyst and 50 cm³ of 0.1M methanolic solution of ortho-chloronitrobenzene and 25 cm³ of distilled water. Then the autoclave was flushed several times with helium followed by flushing with hydrogen in order to remove the air. In each case, the reaction time was 2 h and the stirring rate was 1000 rpm. The reaction products were analysed on a gas chromatograph equipped with a capillary column RESTEK MXT-5. Catalytic measurements carried out with metal-free MgF₂ support proved the inactivity of the support for the reduction of nitric group of o-CNB.

Catalytic test – hydrogenation of toluene

Toluene hydrogenation was performed at atmospheric pressure using a fixed-bed flow reactor and H₂ as carrier gas. Fresh catalyst, after drying (0.025 g) was placed in the reactor and reduced for 2 h in a flow (100 cm³ × min⁻¹) of pure hydrogen (99.99% purchased from Messer) at the range of 300–550°C. The H₂ (50 cm³ × min⁻¹) passed

through a saturator filled with toluene. The concentration of toluene in feed was stable and was $0.75 \text{ mmol} \times \text{cm}^{-3}$. The catalysts were heated at the rate of $10^\circ\text{C} \times \text{min}^{-1}$ and catalytic tests were carried out at $50\text{--}225^\circ\text{C}$ over the same catalyst. The reaction products were analyzed on a gas chromatograph equipped with a capillary column RESTEK MXT-1. The catalytic activity was presented as *apparent rate* calculated by the following Equation:

$$r_t = \frac{FYC}{N} \left[\frac{\text{mol}_{\text{Tl}}}{\text{mol}_{\text{Ru}} \text{ min}} \right]$$

where F is the total flow rate of the feed ($\text{cm}^3 \times \text{min}^{-1}$); Y the fractional conversion; C the concentration of toluene in the feed ($\text{mol}_{\text{Tl}} \times \text{cm}^{-3}$) and N the ruthenium content (mol_{Ru}) in the sample.

RESULTS AND DISCUSSION

Traditional methods of metallic catalysts preparation in which a metal salt is deposited onto a substrate and reduced at a high temperature, do not permit a precise regulation of metal particle size. In order to get control over the size of monodisperse metal particles, we proposed their synthesis in solution by reduction of metal salt with alcohol. The colloids thus obtained were introduced onto the MgF_2 surface by impregnation to get supported metal catalysts of monodisperse distribution of particle size. The monodispersity of metal particles is of profound importance in the reaction of chloronitrobenzene reduction to chloroaniline, as this reaction is structure sensitive and strongly depends on the size of the metal particles of the catalyst. The possibility of control of metal particles monodispersity should permit better control of the activity and selectivity of the catalysts. For the sake of comparison, a ruthenium catalyst was prepared by the conventional method of the support impregnation with a metal salt solution. The present study is the first ever on the application of colloidal Ru/MgF_2 catalyst in the reactions of hydrogenation of ortho-chloronitrobenzene to ortho-chloroaniline and hydrogenation of toluene to methylcyclohexane.

Characterisation of Ru-PVP colloids and catalysts

The structure sensitive reactions are well known to profoundly depend on the size of metal particles. It is rather difficult to obtain monodisperse metal particles by the traditional methods of catalyst preparation such as impregnation or wetting. Thus the idea was to introduce on the support surface colloidal metal particles obtained by chemical reduction in the presence of PVP to get a supported catalyst of high monodispersity of the metallic phase. With the use of solutions of different concentrations of ruthenium chloride, colloids of different size metal particles were obtained. These sizes

were determined from TEM images (Table 2). Figure 1 shows the TEM images (Fig. 1a and c) of colloids R1 and R3 and histograms of metal particle size (Fig. 1b and d). Average size of colloidal particles increases with the rise of ruthenium chloride concentration in the starting solution (Table 1) from 1.6 to 2.6 nm (Table 2). The obtained colloids were deposited on the surface of magnesium fluoride by the method of impregnation. After drying the catalysts were reduced under hydrogen flow at 400°C . The XRD study of supported catalysts showed that determination of Ru particle size was impossible, because of no reflections from ruthenium metal in the X-ray patterns, which points to very small sizes of the particles.

Interesting results were obtained while studying H_2 chemisorption on colloidal Ru/MgF_2 catalysts (Table 2). The size of colloidal particles calculated on the basis of chemisorbed hydrogen quantities appeared to be by one order of magnitude higher than that determined on the basis of TEM investigation. This is due to the retardation of hydrogen chemisorption. This phenomenon can follow from a strong metal-support interaction (SMSI). A stronger retardation of hydrogen chemisorption observed for the R1/F catalyst, when compared to those of R3/F and R5/F catalysts, results from smaller sizes of ruthenium particles. It is illustrated schematically in Figure 2. The percentage of Ru atoms "poisoned" by neighbouring fluoride ions is higher in smaller particles than in large crystallites, hence the former chemisorb less hydrogen. The phenomenon of chemisorption damping has been earlier observed for the conventional Ru/MgF_2 catalysts³⁵, whose FTIR spectra of adsorbed CO confirmed the presence of ruthenium centres with partial positive charge ($\text{Ru}^{\text{d}+}$). Strong interactions of Ru crystallites with MgF_2 surface were confirmed by EPR study at the liquid helium temperature³⁶. The EPR results proved that even after the reduction in hydrogen atmosphere at 400°C ruthenium (III) is present on the catalyst surface. It is supposed that also for the colloidal Ru/MgF_2 catalysts, ruthenium strongly interacts with the support surface which is the reason for hydrogen chemisorption damping.

Hydrogenation activity

Colloidal Ru/MgF_2 catalysts were tested in reactions of hydrogenation of ortho-chloronitrobenzene to ortho-chloroaniline (Fig. 3a) and hydrogenation of toluene to methylcyclohexane (Fig. 3b). Catalytic tests in the

Table 2. Diameter of ruthenium particles [nm]

Sample	TEM, (for colloids)	H_2 chemisorption, (for catalysts)	XRD, (for catalysts)
R1/F	1.6	136	Not detected
R3/F	2.3	32	Not detected
R5/F	2.6	27	Not detected

Table 1. Catalyst characterization – symbol, precursor and pre-treatment condition

Colloid label	Concentration of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{mmol} \cdot \text{dm}^{-3}$	PVP*/Ru, mole ratio	Catalyst label	Method of activation
R1	1	20:1	R1/F	dried at 80°C reduction at 400°C
R3	3	20:1	R3/F	dried at 80°C reduction at 400°C
R5	5	20:1	R5/F	dried at 80°C reduction at 400°C

*PVP – Polyvinylpyrrolidone, average mol wt = 19 000; F – Magnesium fluoride – calcined at 400°C for 4 h.

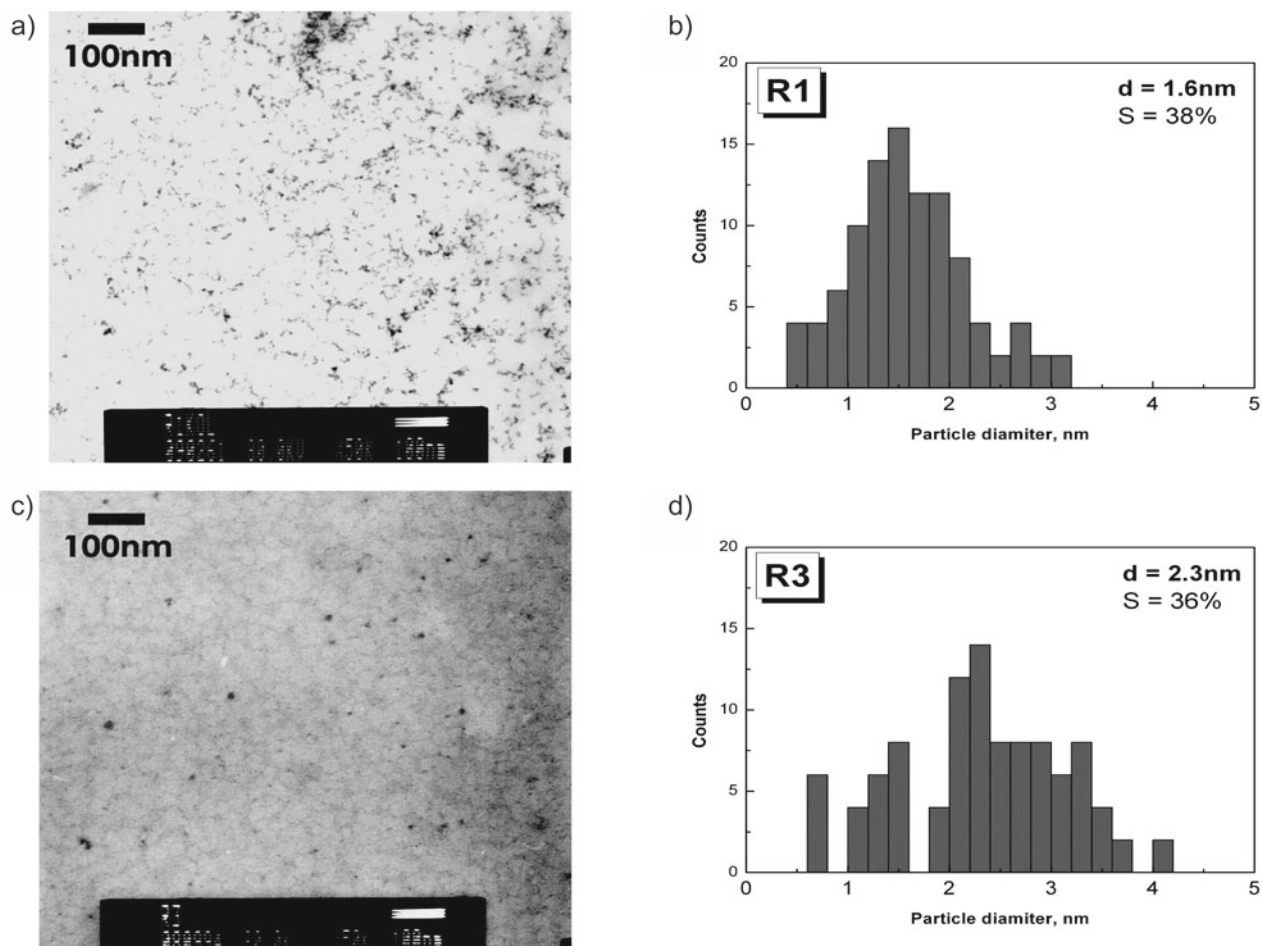


Figure 1. TEM micrographs (a and c) and corresponding particle size distribution histograms (b and d) of PVP-stabilised ruthenium colloids

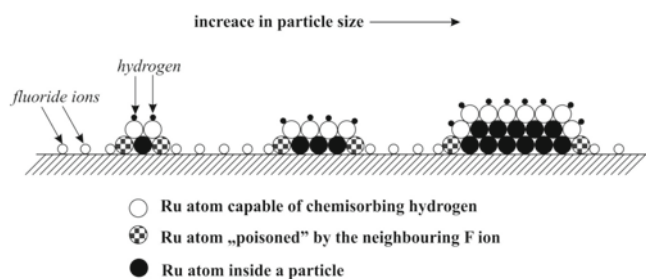


Figure 2. The proposed mechanism of hydrogen chemisorption retardation on Ru-nanoparticles supported on MgF_2 surface

reaction of selective reduction of *o*-chloronitrobenzene to *o*-chloroaniline were carried out in a batch reactor at 70°C under pressure of 4 MPa for 2 hours. Optimum reaction conditions were established on the basis of results reported in¹⁵. The activity and selectivity of colloidal ruthenium catalysts are presented in Figure 3a. The activity of the catalysts was compared with that of the conventional system obtained by the impregnation of MgF_2 with ruthenium(III) chloride solution. The ruthenium colloidal catalyst supported on MgF_2 (Ru1/F) is almost three times more active in the reduction of nitric group of *o*-CNB than conventional Ru/MgF_2 (conversion $\sim 30\%$). Catalytic activity was increasing with decreasing size of colloidal Ru particles (Table 2, TEM results), from 59% for R5/F to 91% R1/F conversion of *o*-chloronitrobenzene to *o*-chloroaniline. However, no changes in the selectivity of hydrogenation of *o*-CNB to

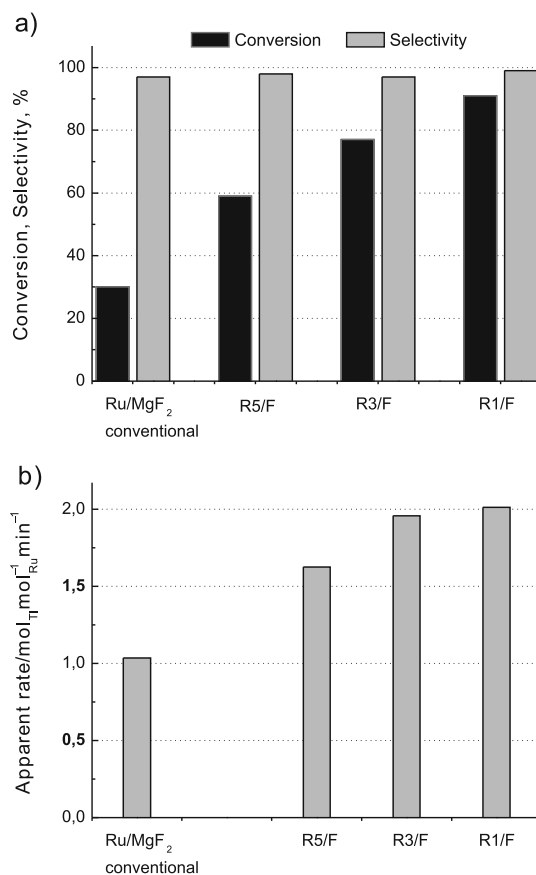


Figure 3. Hydrogenation properties of the colloidal Ru/MgF_2 catalysts. a) hydrogenation of *o*-CNB; b) hydrogenation of toluene

o-CAN were observed. It remained at over 97%, reaching 99% for the most active catalyst R1/F.

A similar tendency of increasing catalytic activity with decreasing size of colloidal Ru particles has been observed for hydrogenation of toluene. The colloidal catalysts showed twice higher activity than the conventional Ru/MgF₂. In all catalytic tests the only product was methylcyclohexane.

CONCLUSIONS

1. The application of the chemical reduction method for catalyst preparation enables obtaining ruthenium nanoparticles of 1.6–2.6 nm in size and a high monodispersity.

2. Ruthenium nanoparticles interact strongly with MgF₂ surface which influences chemisorption and catalytic properties of colloidal Ru/MgF₂ catalysts.

3. Colloidal nanoparticles supported on MgF₂ surface permit getting a catalyst of higher activity and selectivity than those observed for the catalysts prepared by using the conventional impregnation technique in the reduction of chloronitrobenzene to aniline and in hydrogenation of toluene to methylcyclohexane.

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